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Kosemura et al.

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(54) **DIE HEAD APPARATUS, COATING METHOD, AND LAMINATED BODY FORMING APPARATUS**

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B05D 1/26 (2006.01)
(Continued)

(52) **U.S. Cl.**
CPC ***B05C 5/0245*** (2013.01); ***B05C 11/023*** (2013.01); ***B05D 1/26*** (2013.01);
(Continued)

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CPC B05C 5/0245; B05C 11/02–023; B05C 11/04–048
See application file for complete search history.

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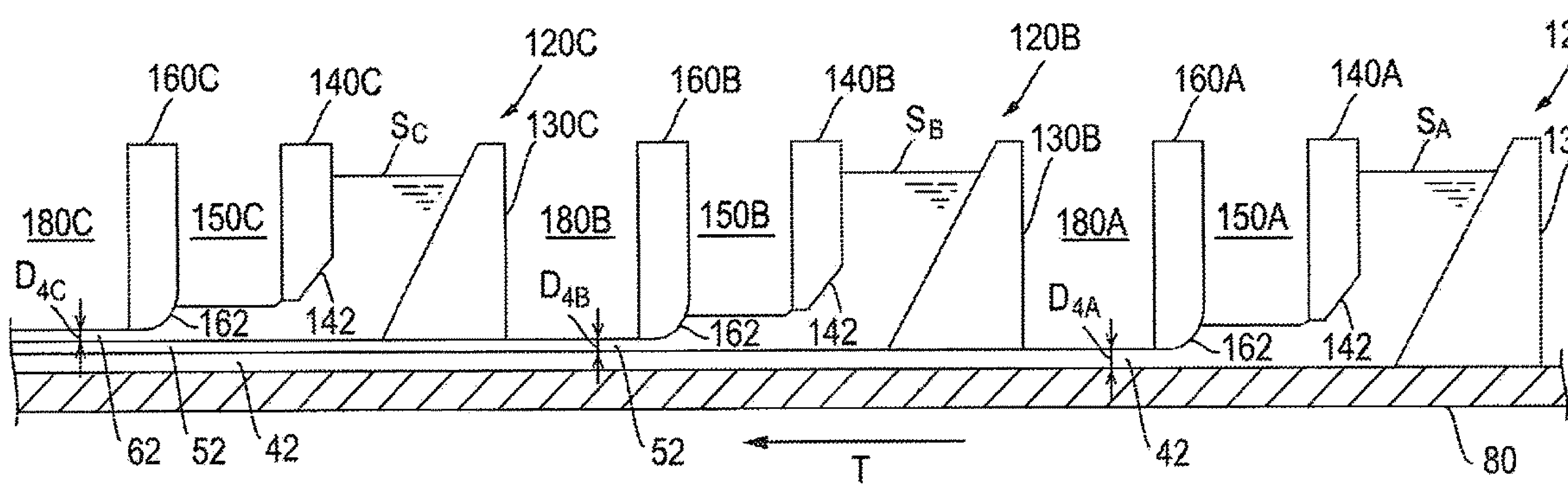
Primary Examiner — Dah-Wei D. Yuan
Assistant Examiner — Stephen A Kitt
(74) *Attorney, Agent, or Firm* — Global IP Counselors, LLP

(57) **ABSTRACT**

A die head apparatus is provided with a front blade, a rear blade, a center blade, and an internal impurity removal space. The front blade and the center blade are configured to form a pool of a slurry. The internal impurity removal space is positioned between the center blade and the rear blade. A distance separating the rear blade and the substrate is set to be smaller than the distance separating the center blade and the substrate.

18 Claims, 18 Drawing Sheets



(51) **Int. Cl.**
B05D 1/42 (2006.01)
B05C 11/02 (2006.01)
H01M 4/04 (2006.01)
H01M 4/88 (2006.01)
H01M 8/124 (2016.01)

(52) **U.S. Cl.**
CPC ***B05D 1/42*** (2013.01); ***H01M 4/0409*** (2013.01); ***H01M 4/0411*** (2013.01); ***H01M 4/8828*** (2013.01); ***H01M 8/124*** (2013.01)

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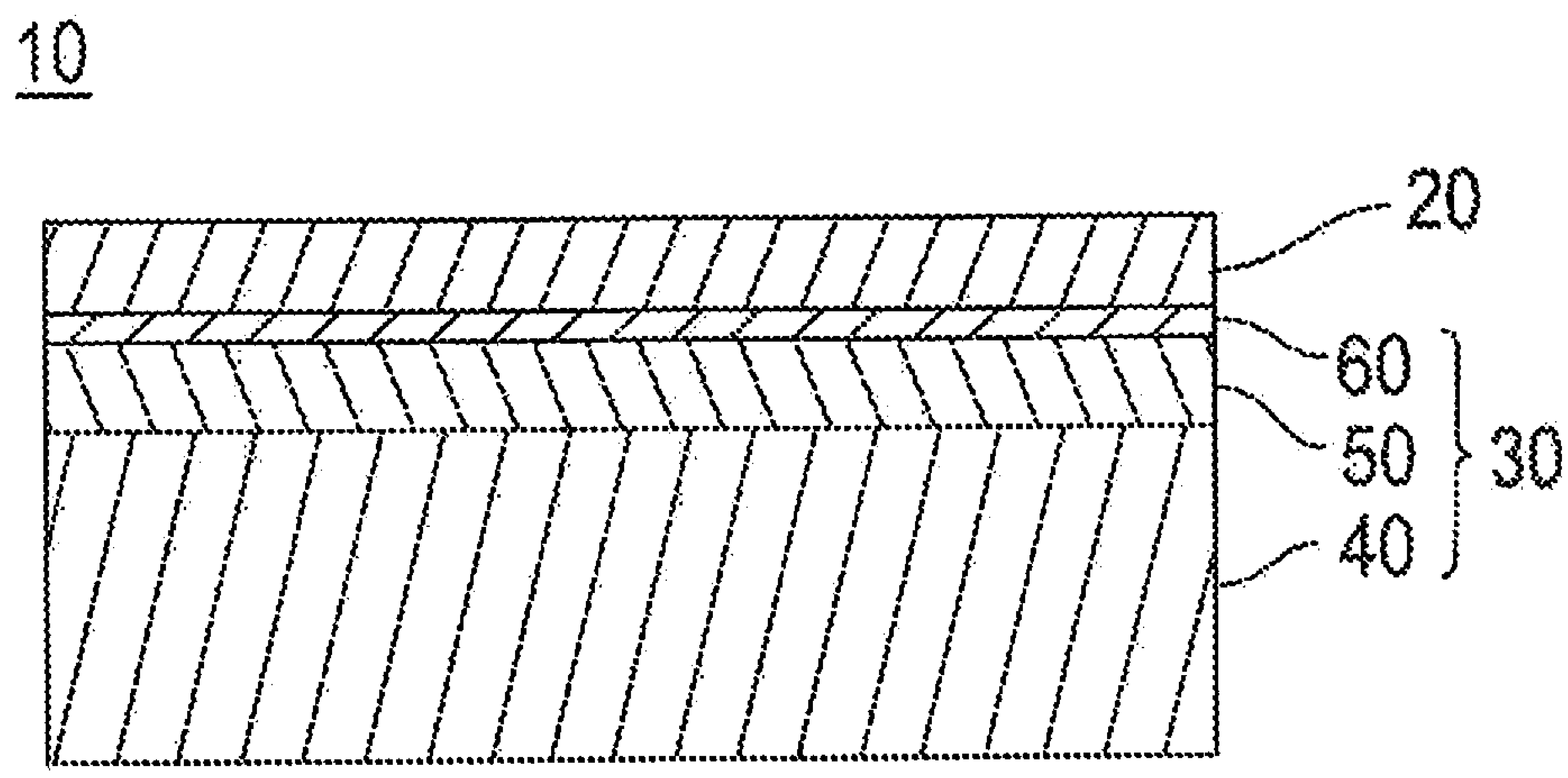

FIG. 1

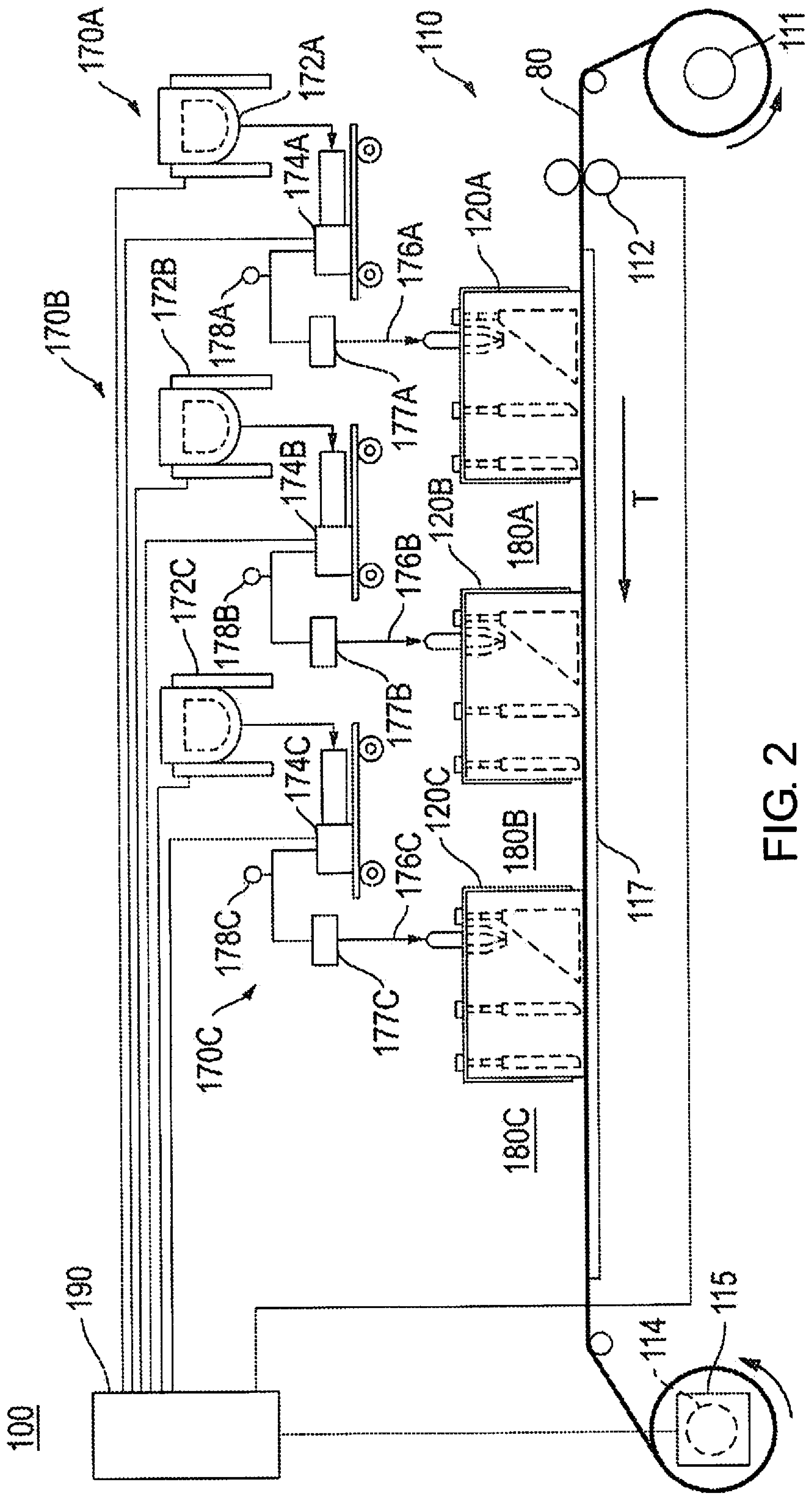
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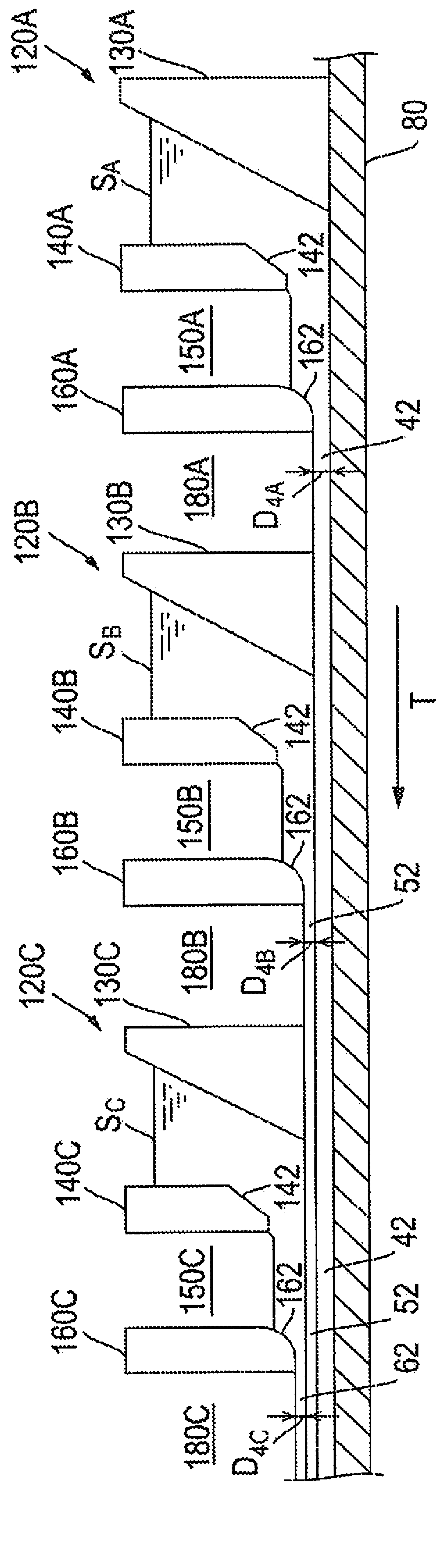
FIG. 2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150B
160B
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180B
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D_{4C}

FIG. 3

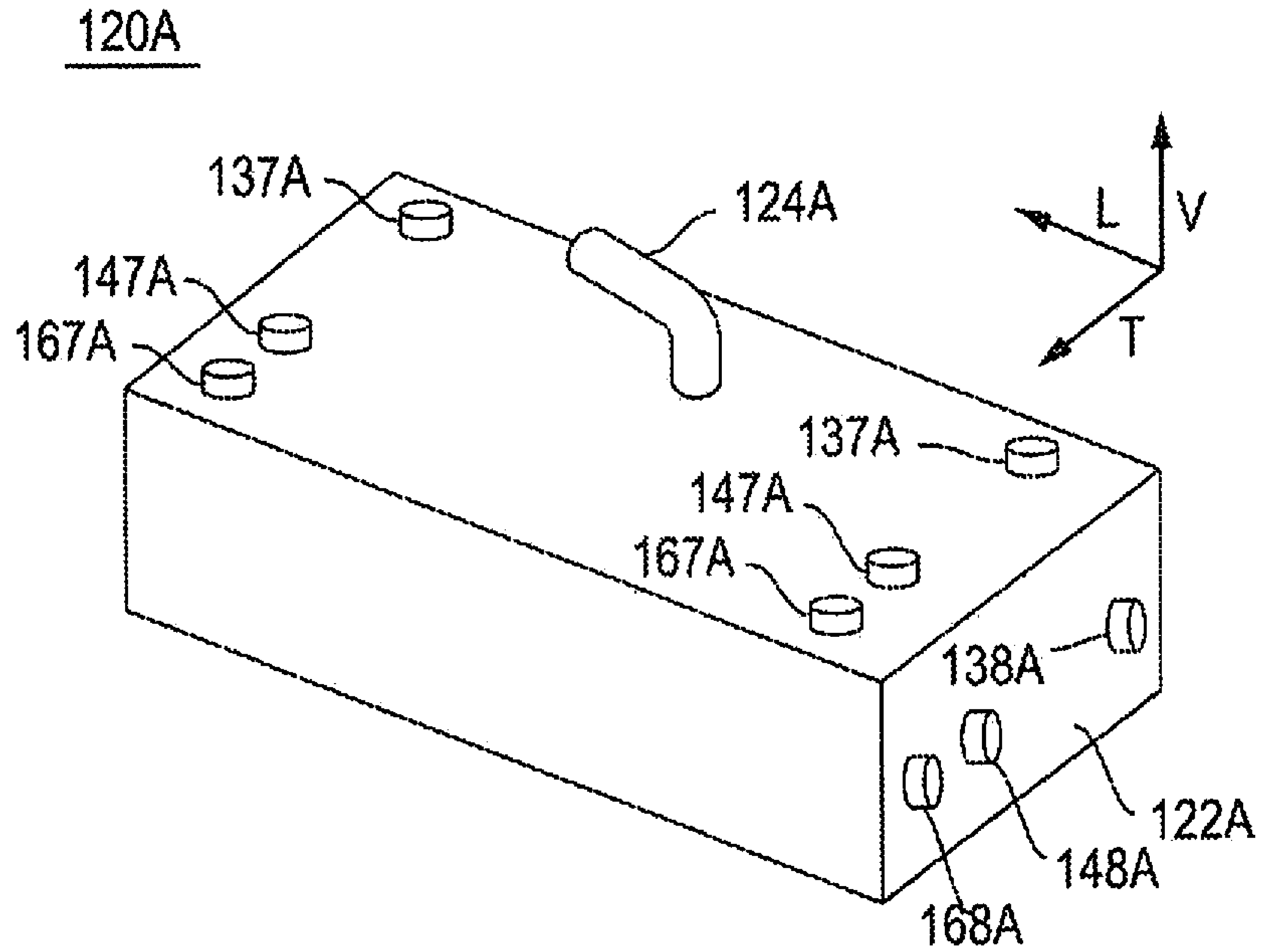
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FIG. 4

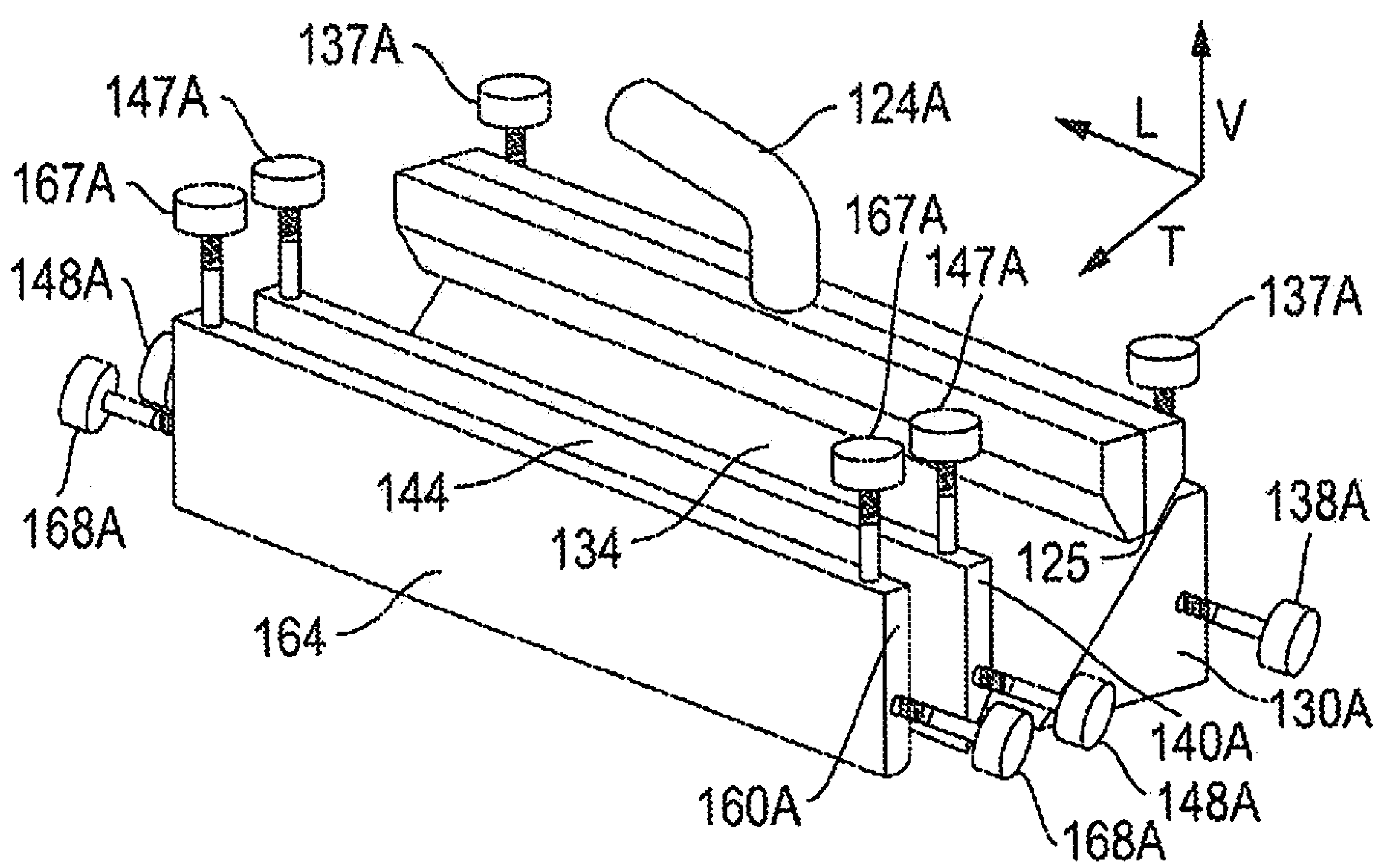
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FIG. 5

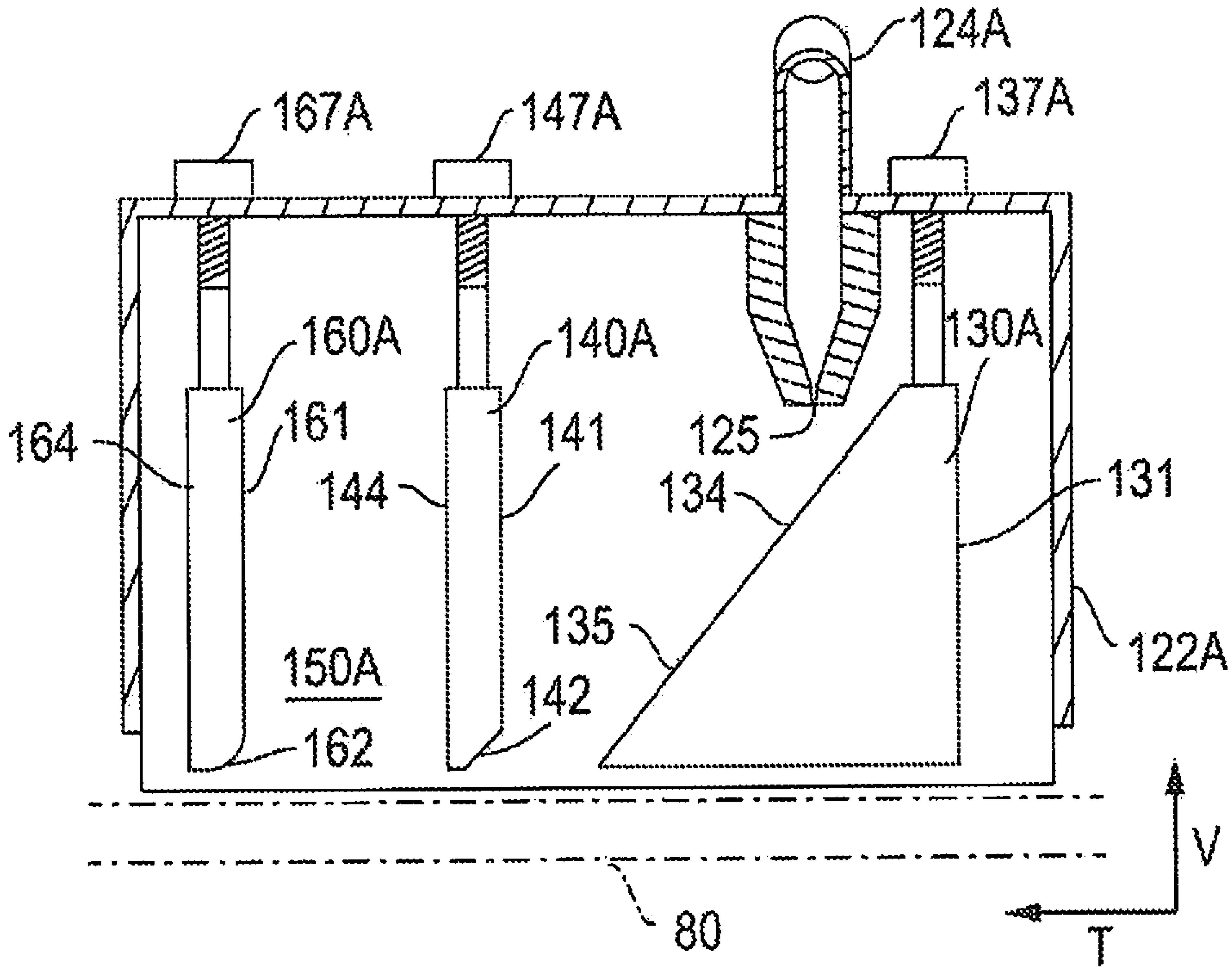
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FIG. 6

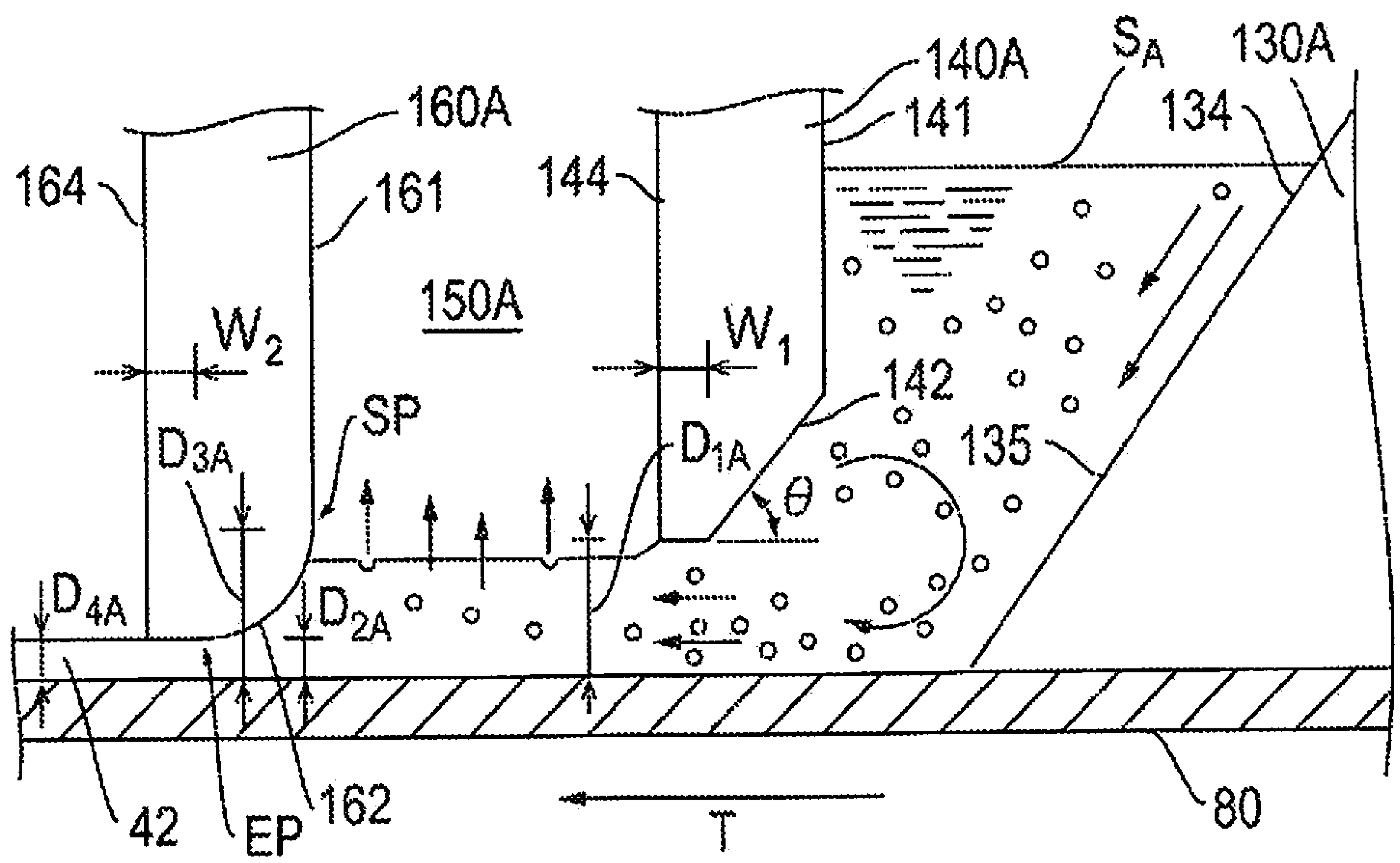
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FIG. 7

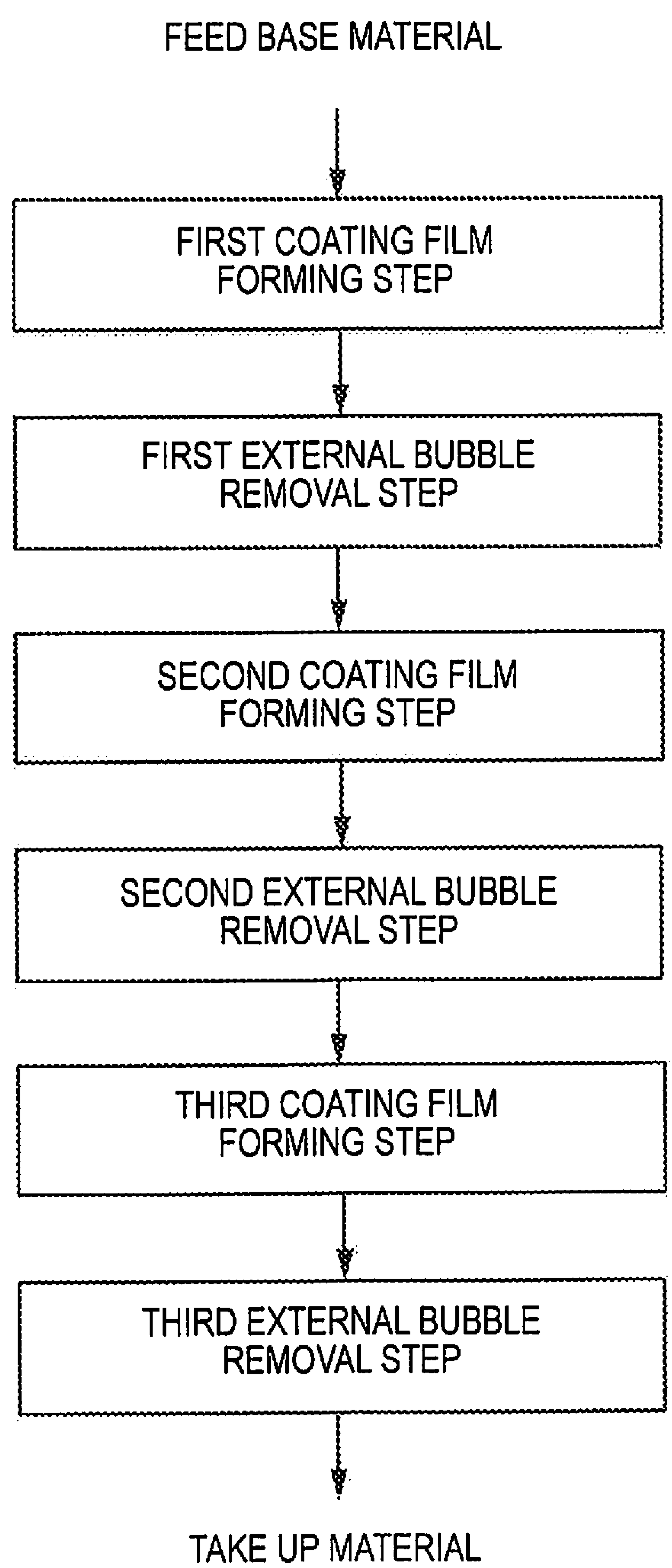
FEED BASE MATERIAL
FIRST COATING FILM FORMING STEP
FIRST EXTERNAL BUBBLE REMOVAL STEP
SECOND COATING FILM FORMING STEP
SECOND EXTERNAL BUBBLE REMOVAL STEP
THIRD COATING FILM FORMING STEP
THIRD EXTERNAL BUBBLE REMOVAL STEP
TAKE UP MATERIAL

FIG. 8

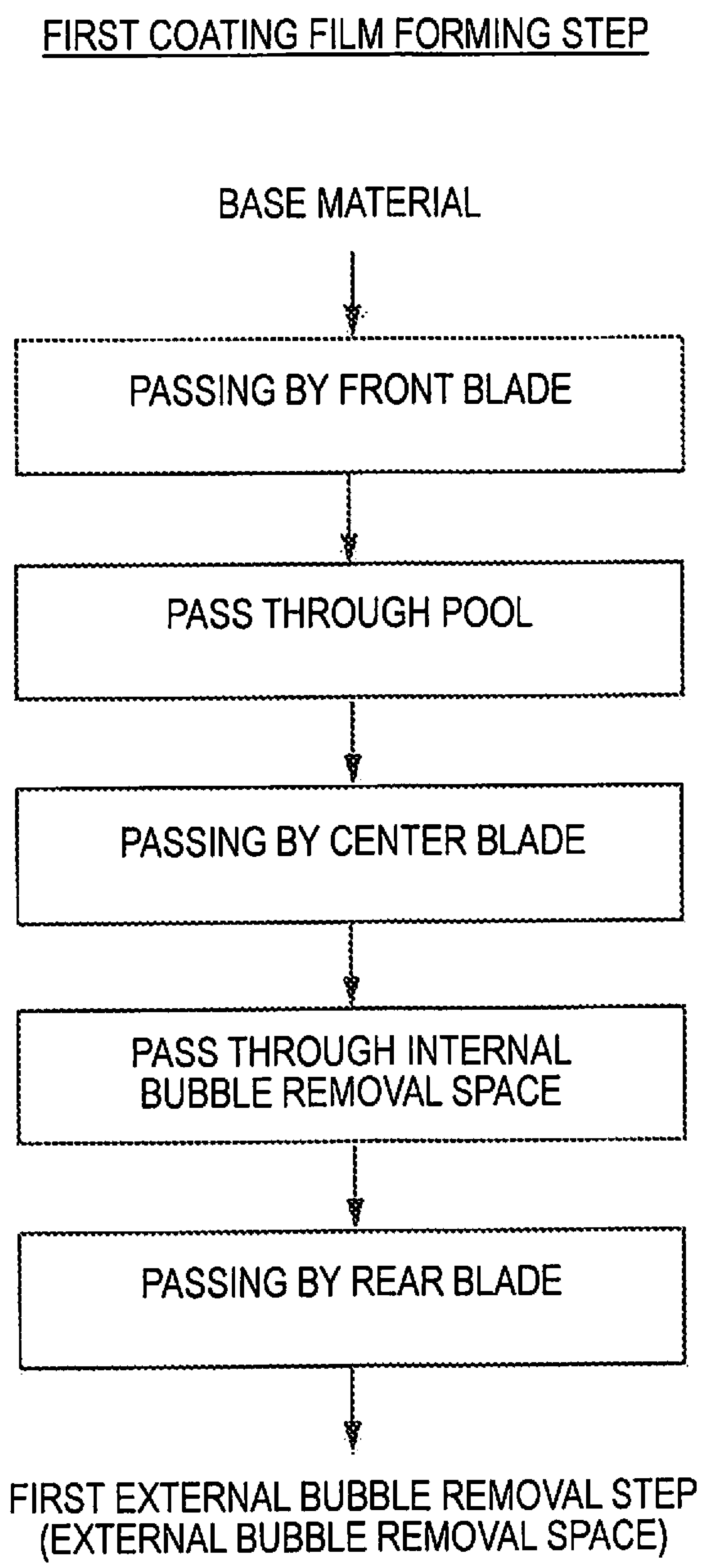
FIRST COATING FILM FORMING STEP
BASE MATERIAL
PASSING BY FRONT BLADE
PASS THROUGH POOL
PASSING BY CENTER BLADE
PASS THROUGH INTERNAL BUBBLE REMOVAL SPACE
PASSING BY REAR BLADE
FIRST EXTERNAL BUBBLE REMOVAL STEP (EXTERNAL BUBBLE REMOVAL SPACE)

FIG. 9

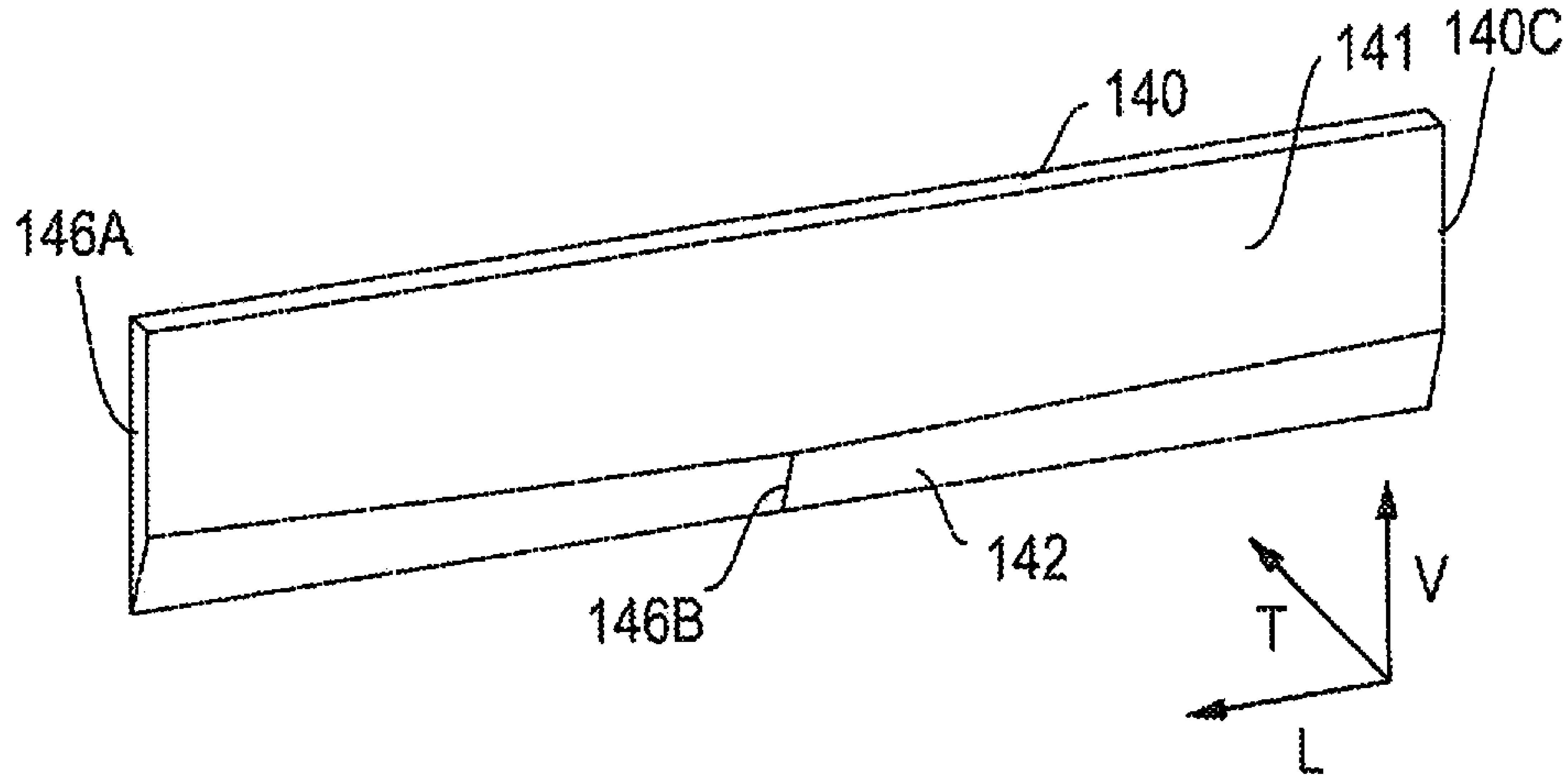

FIG. 10A

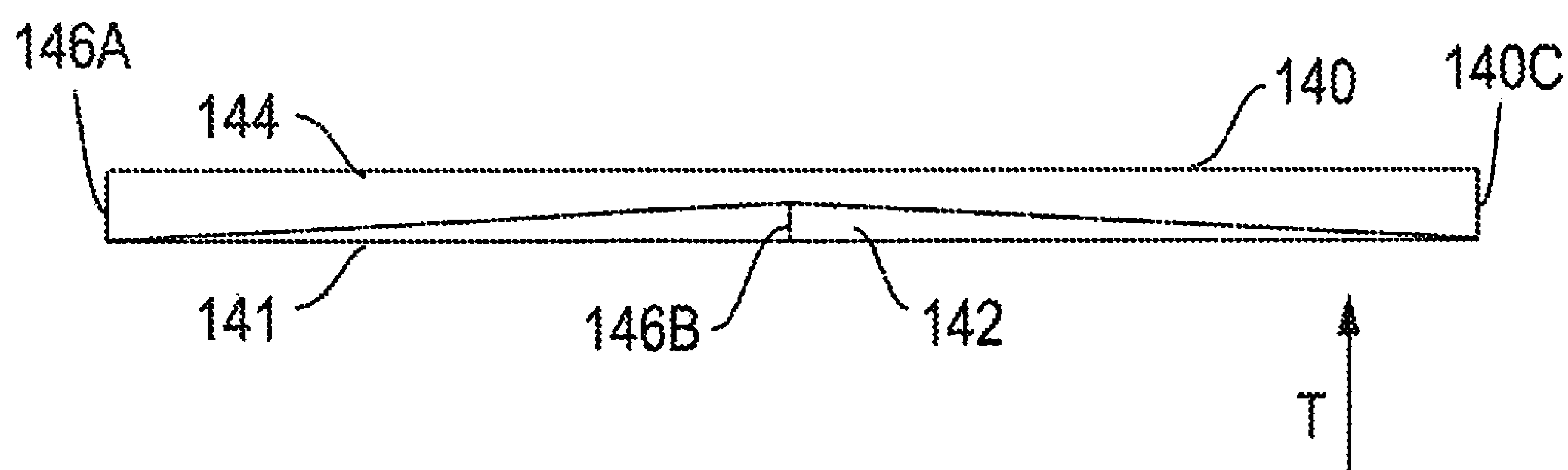

FIG. 10B

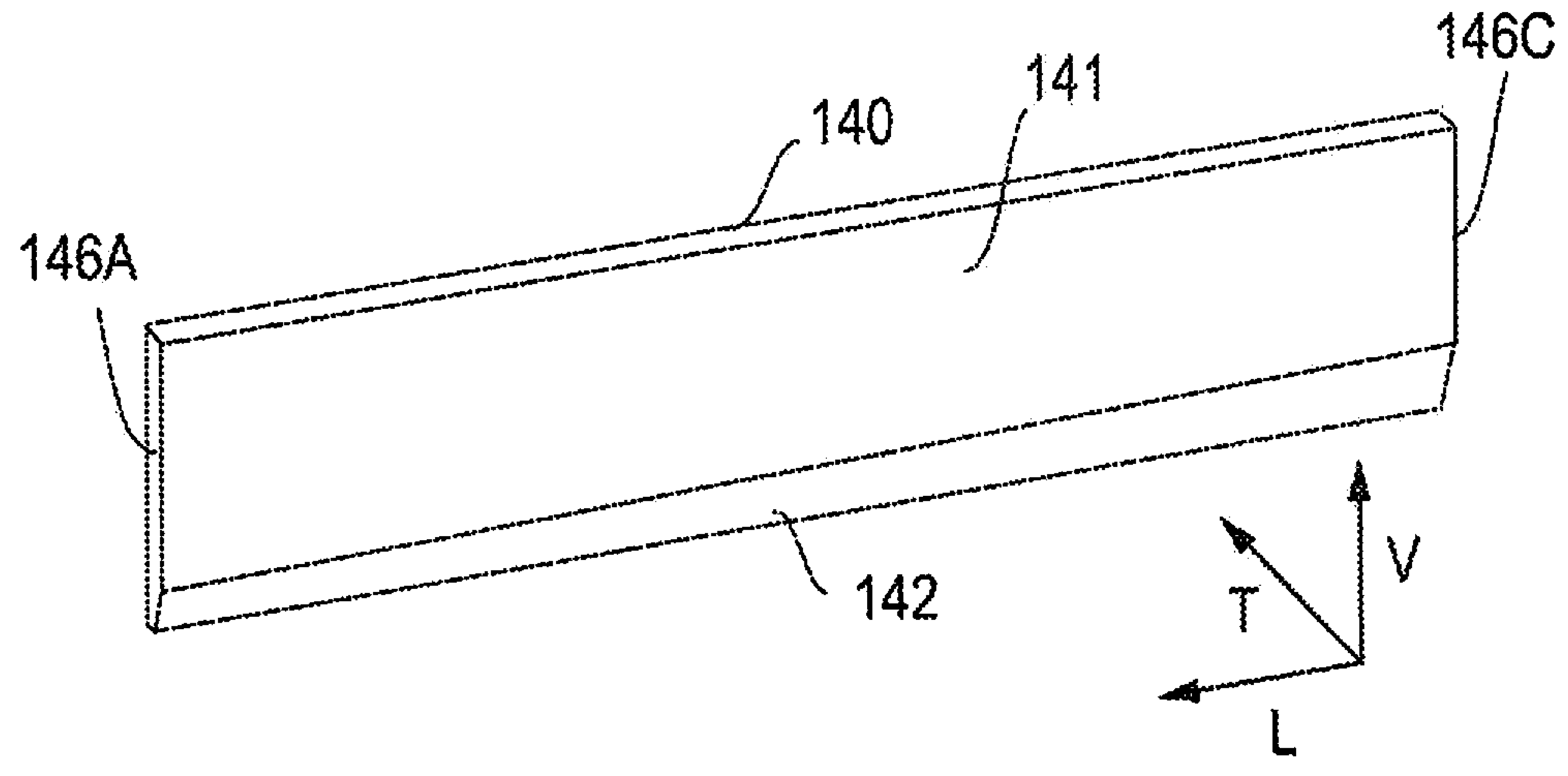

FIG. 11A

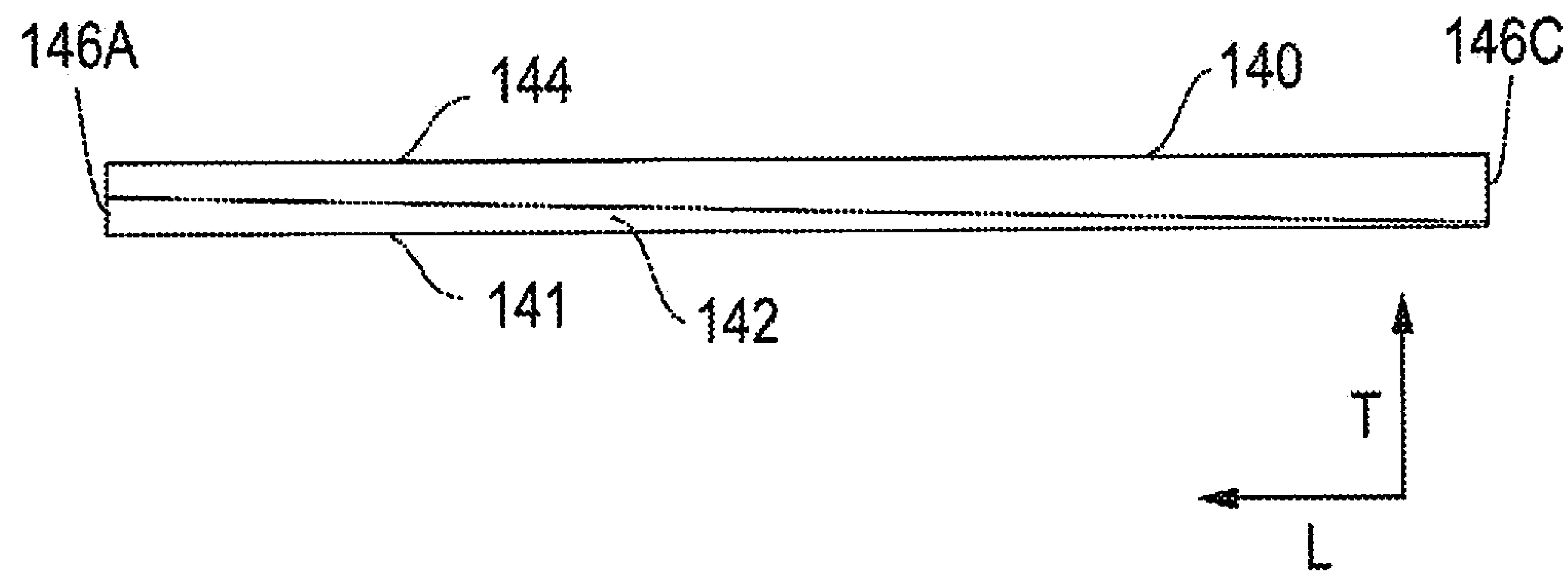

FIG. 11B

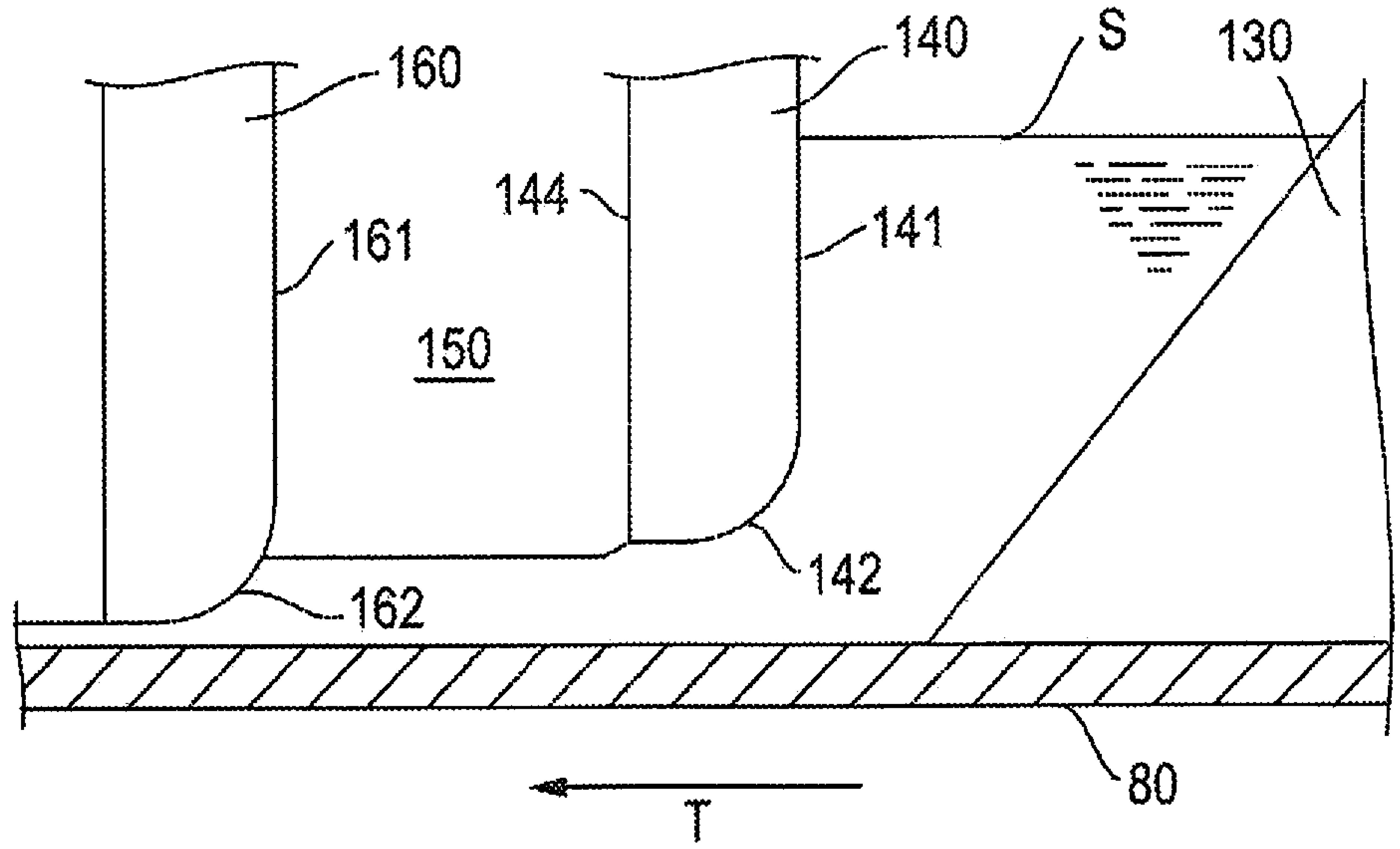
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FIG. 12

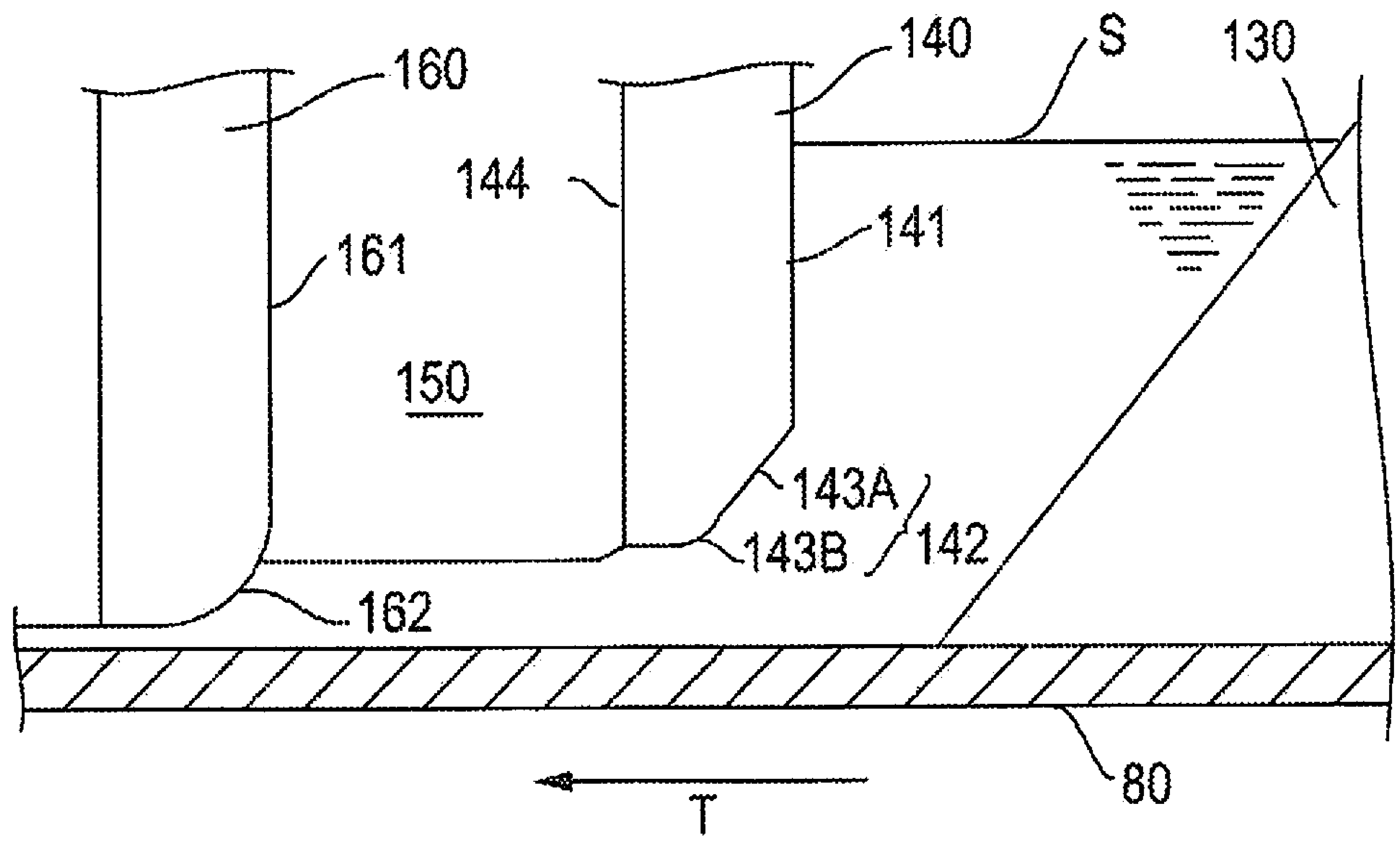
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FIG. 13

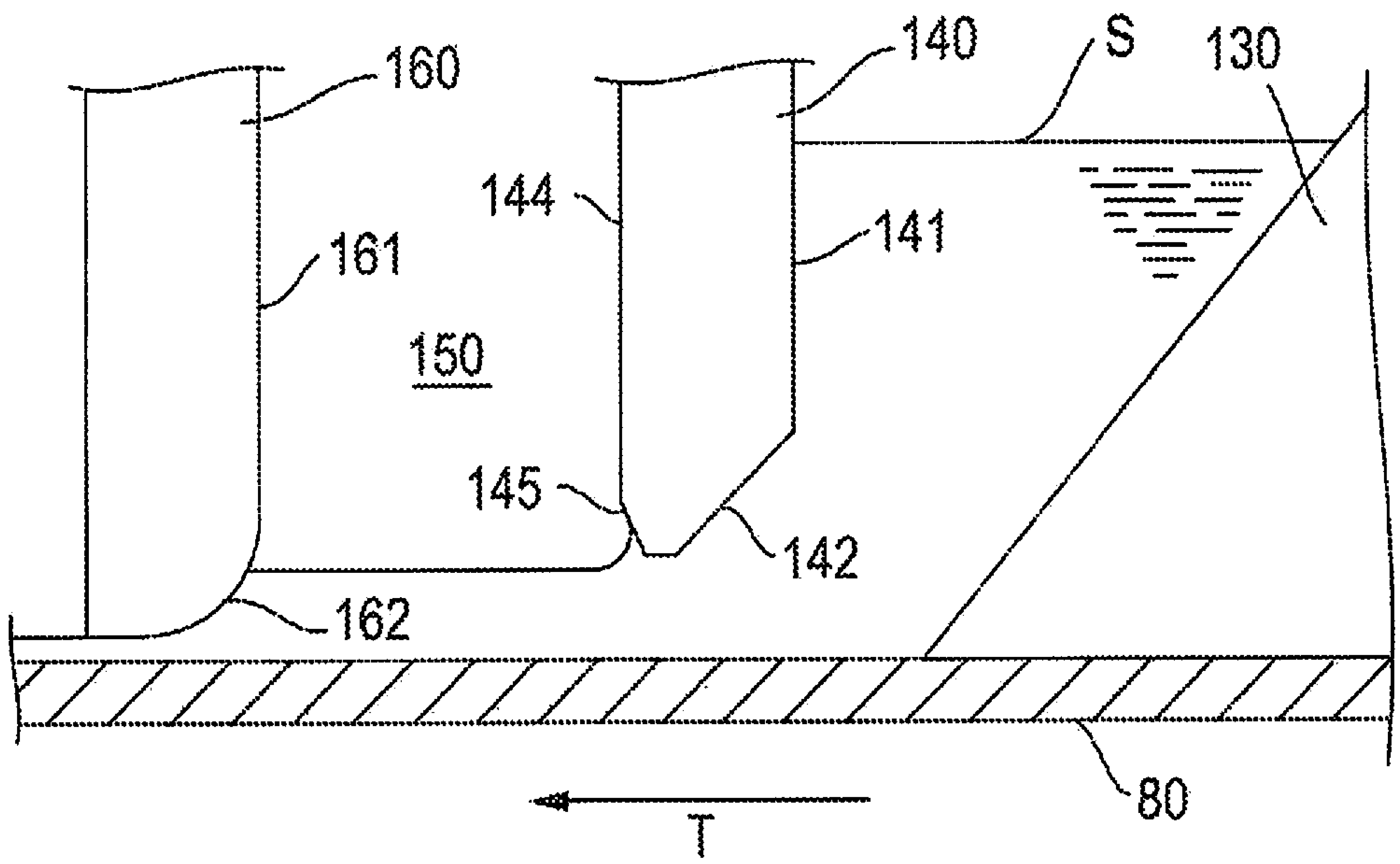
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FIG. 14

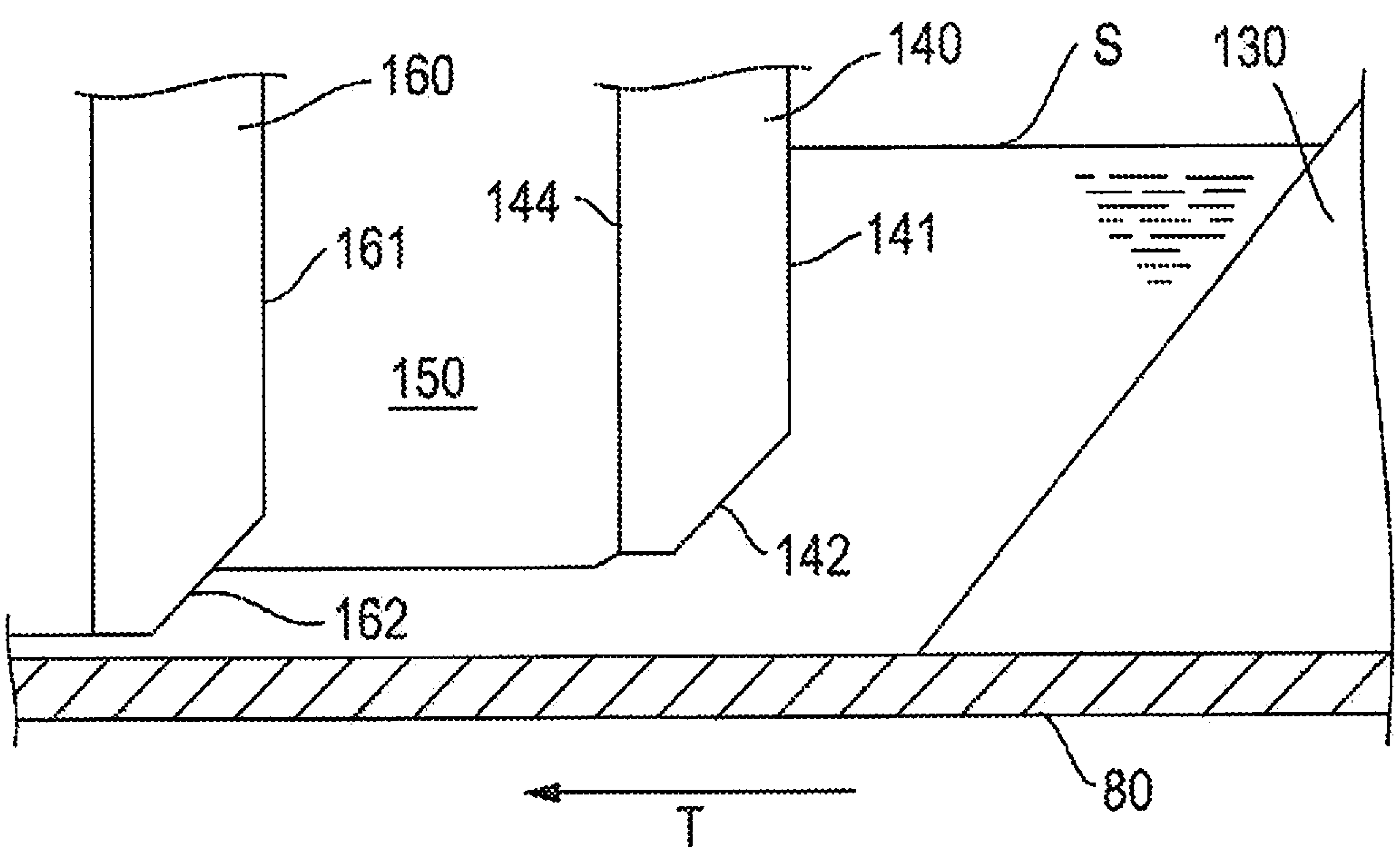
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FIG. 15

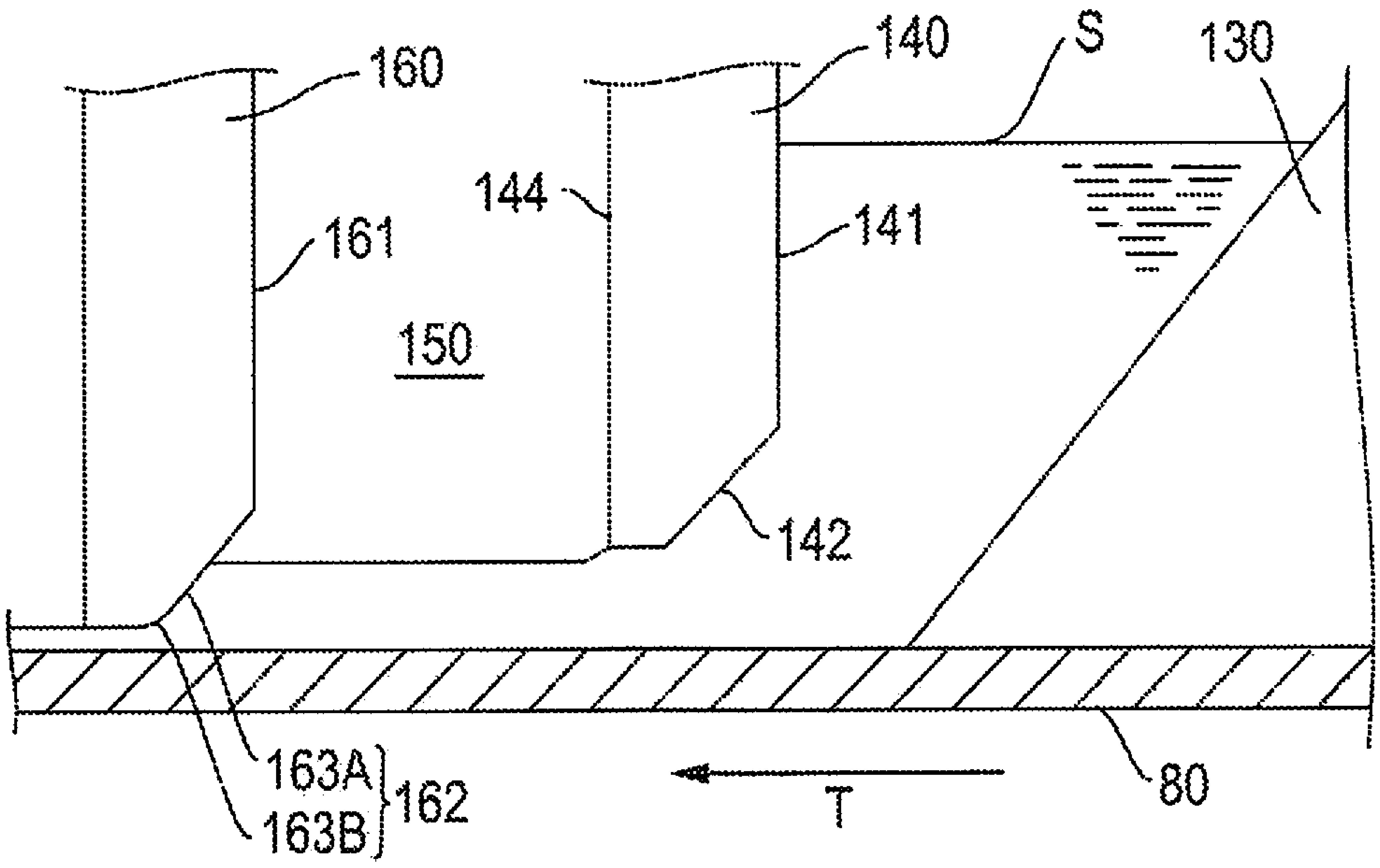
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FIG. 16

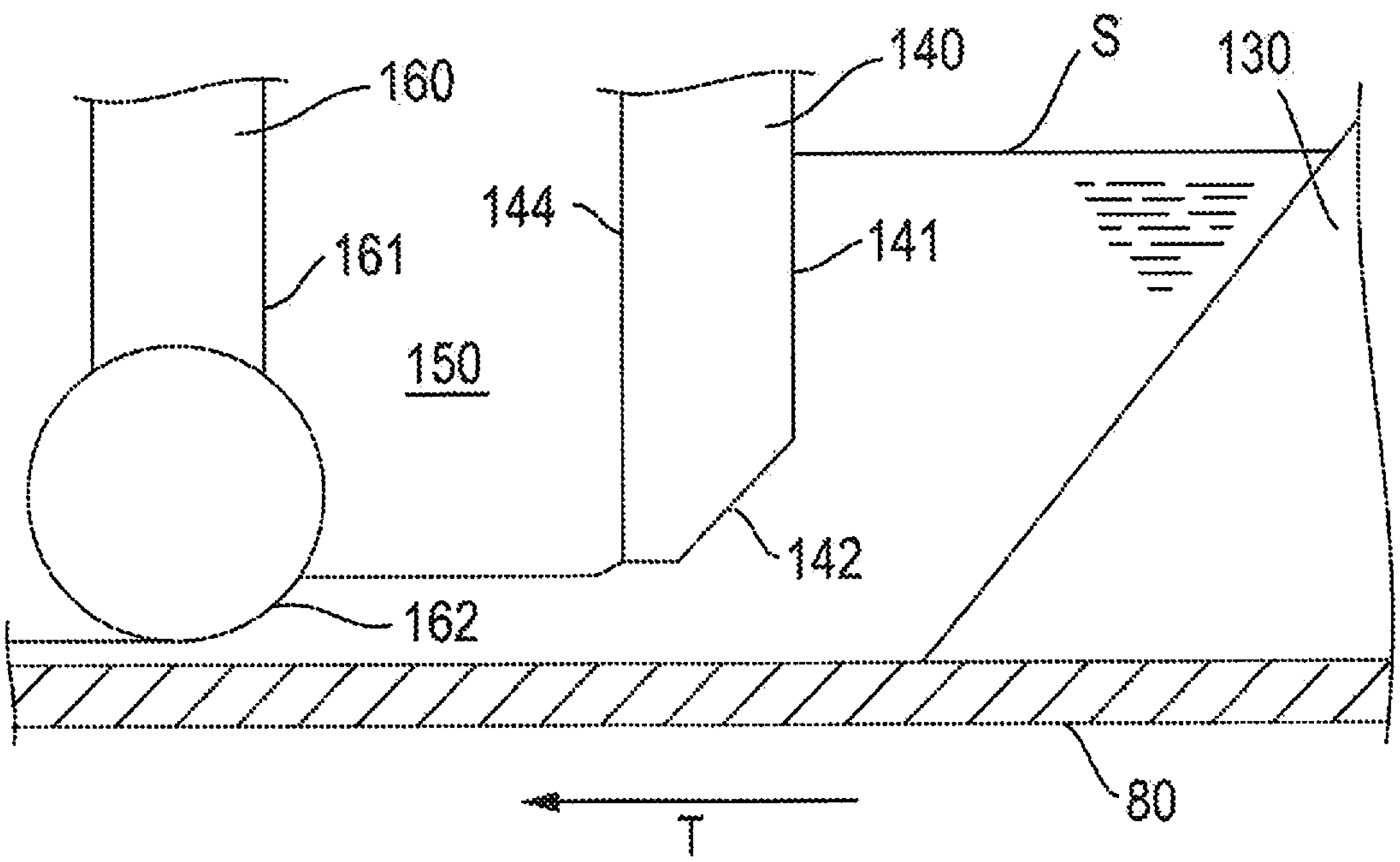
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FIG. 17

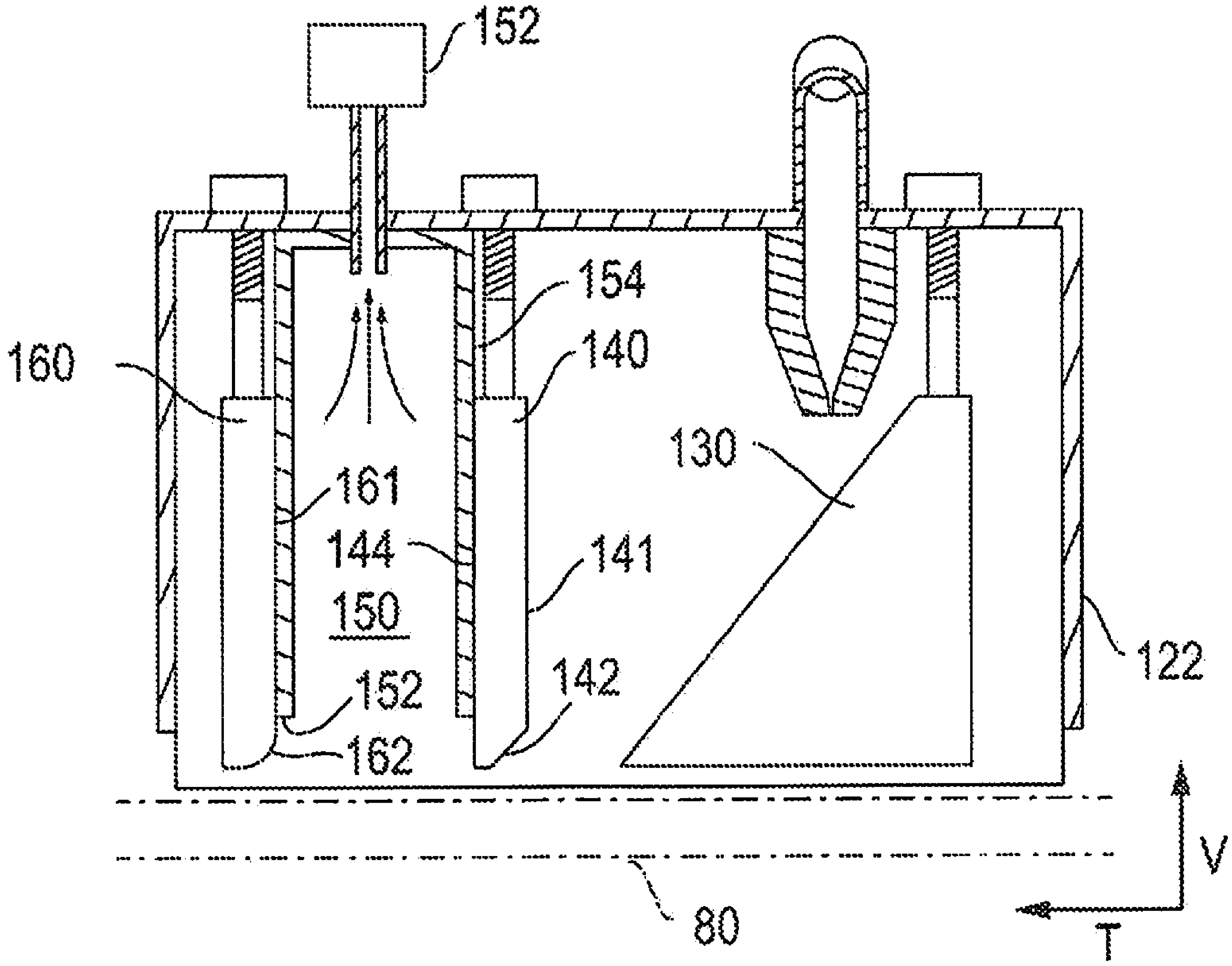

FIG. 18

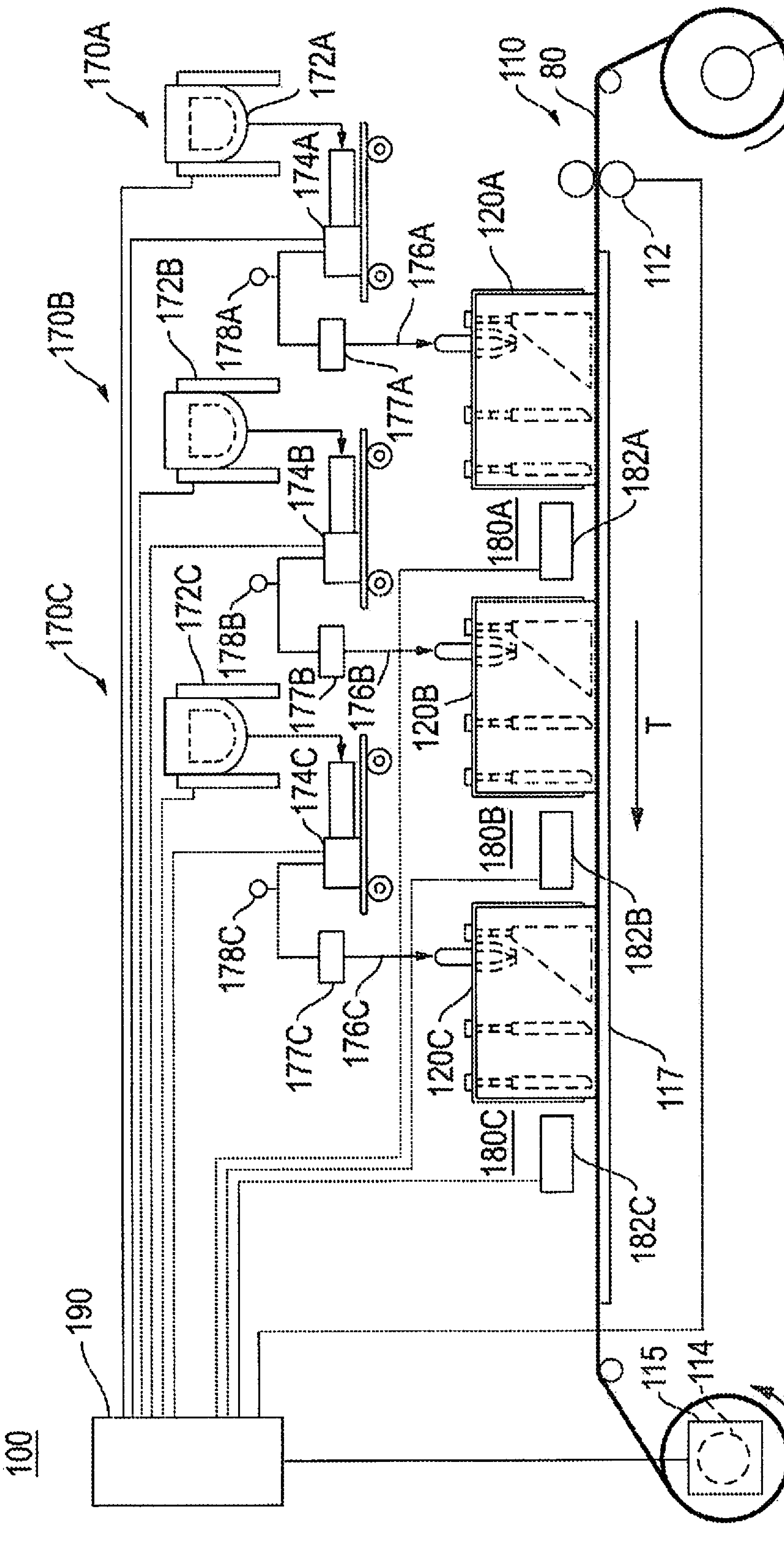

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FIG. 19

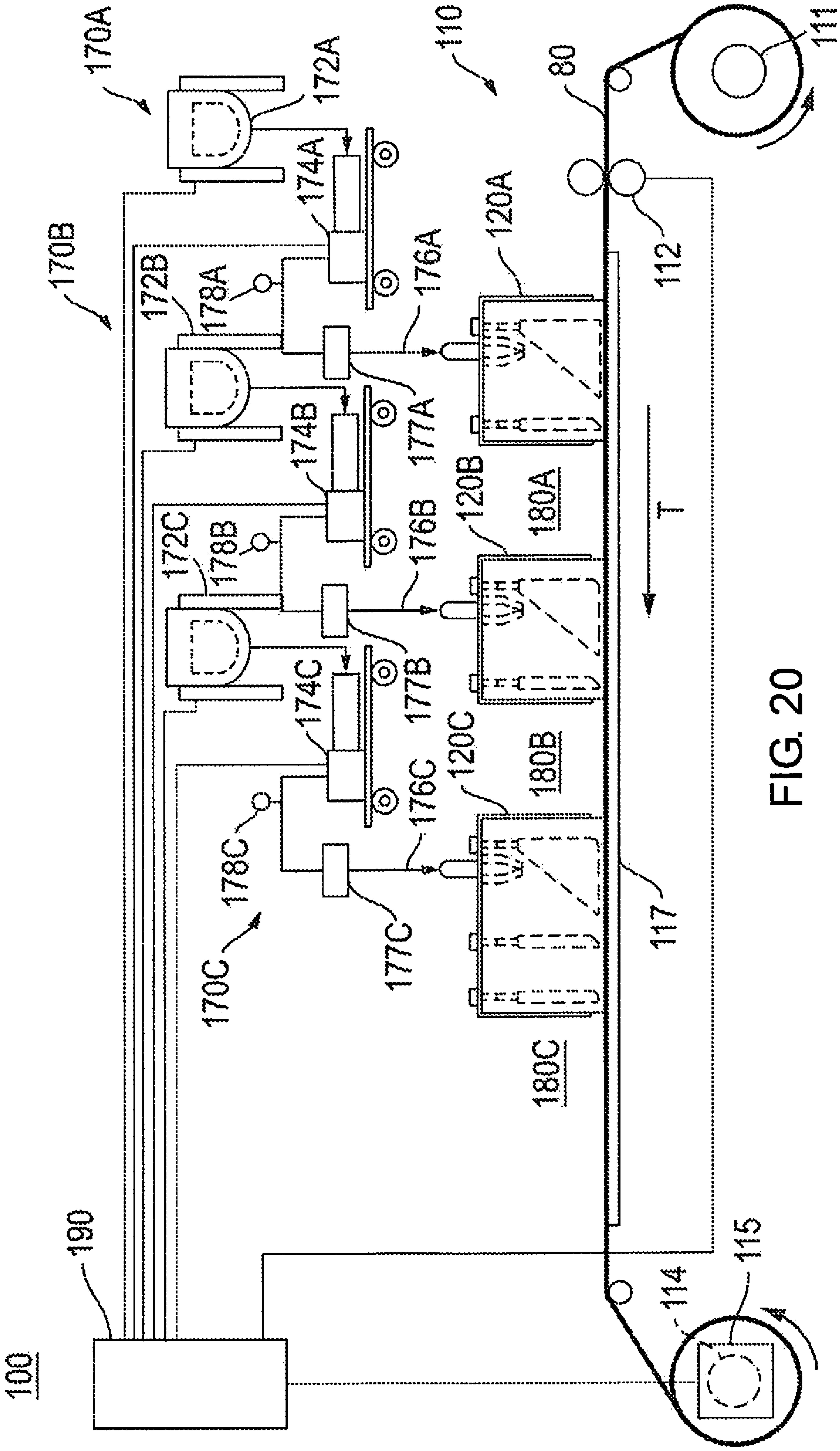

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FIG. 20

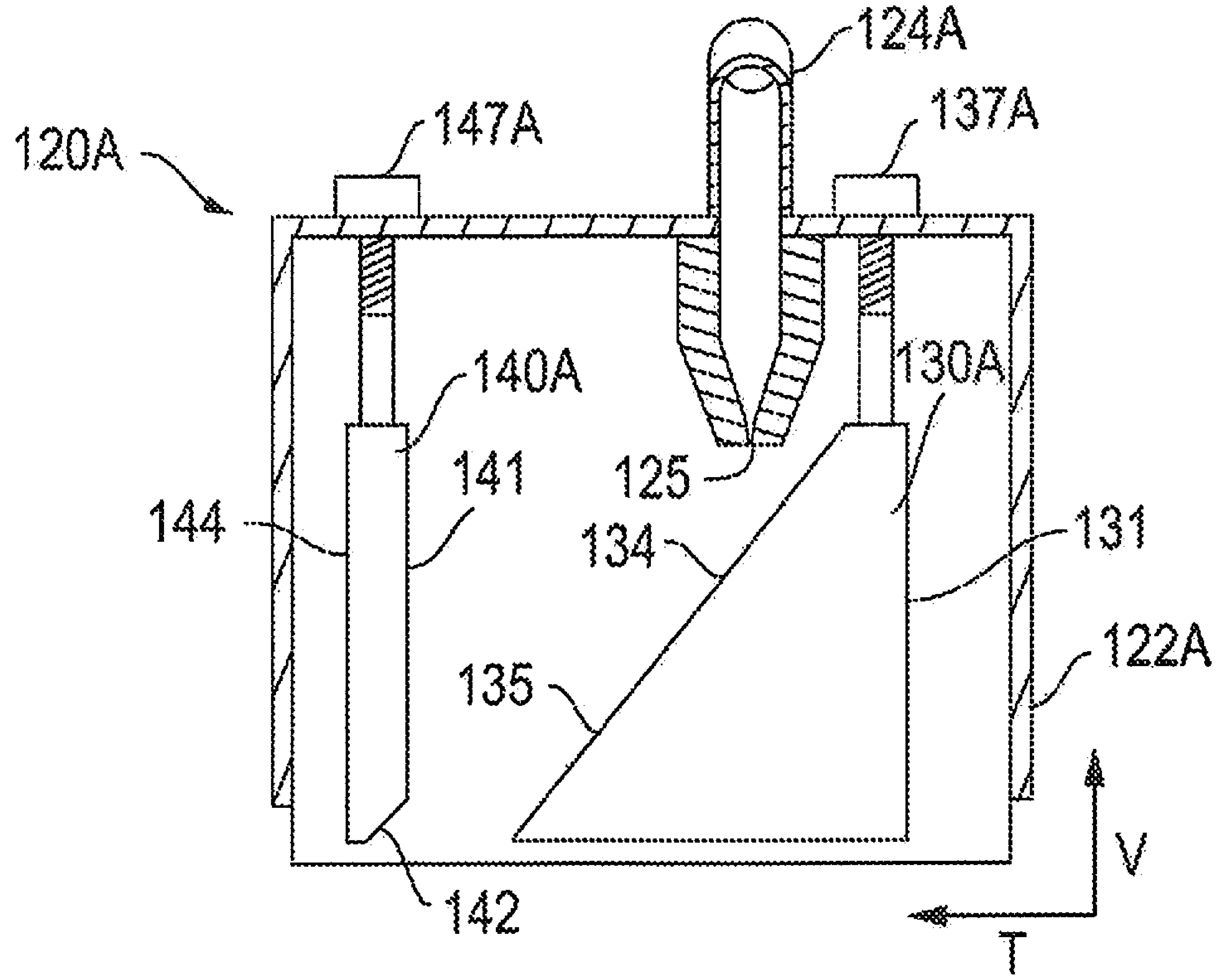

FIG. 21A

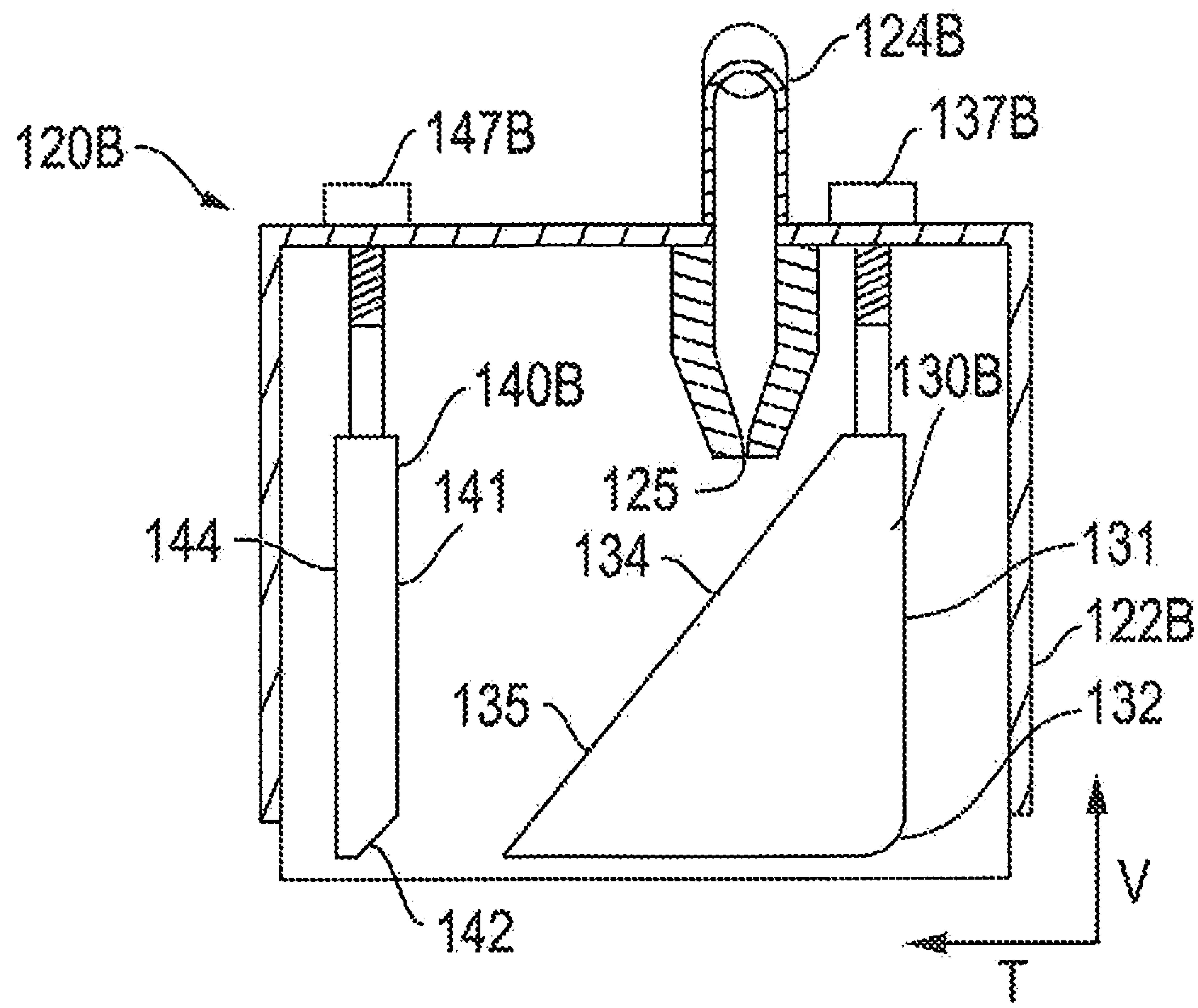

FIG. 21B

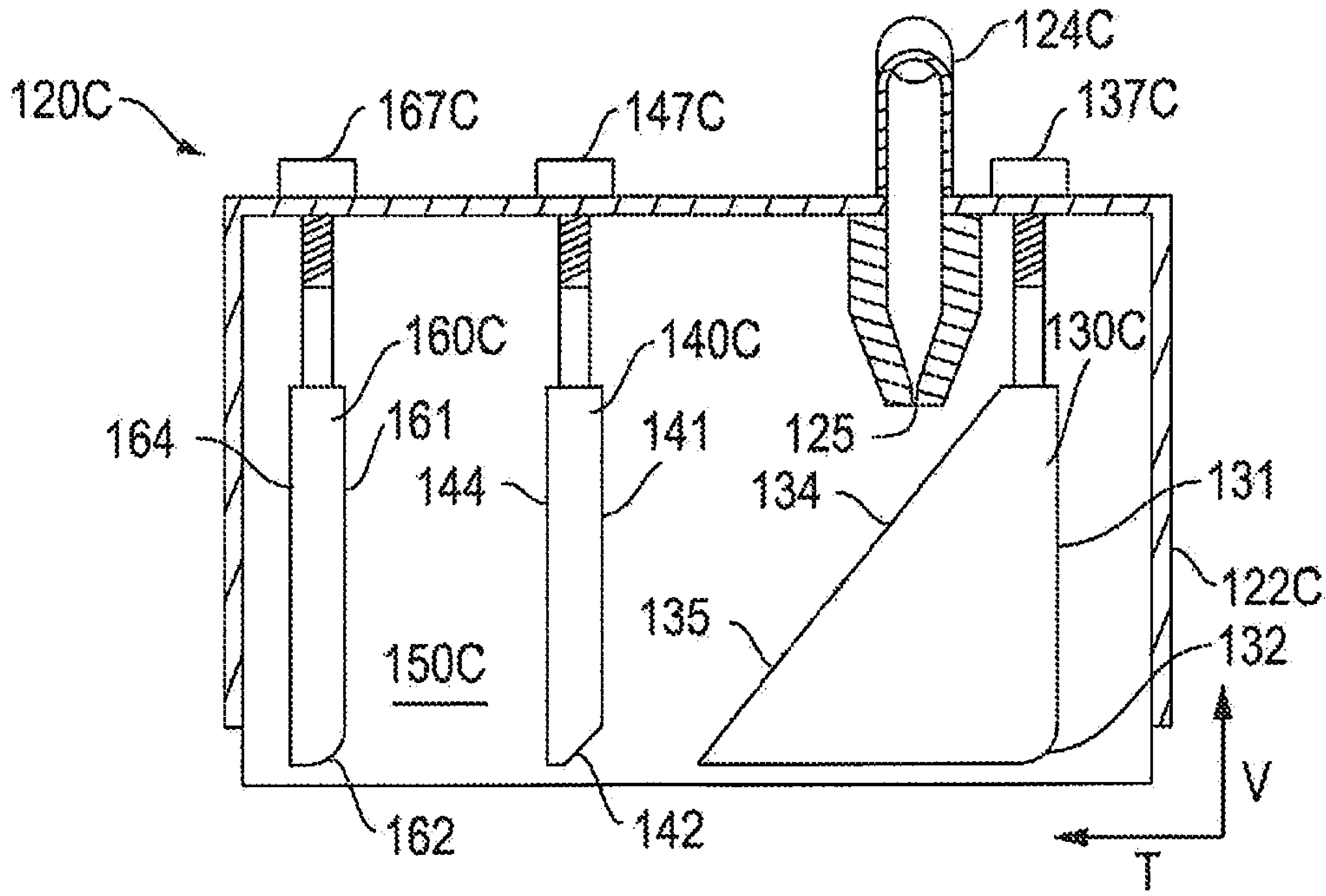
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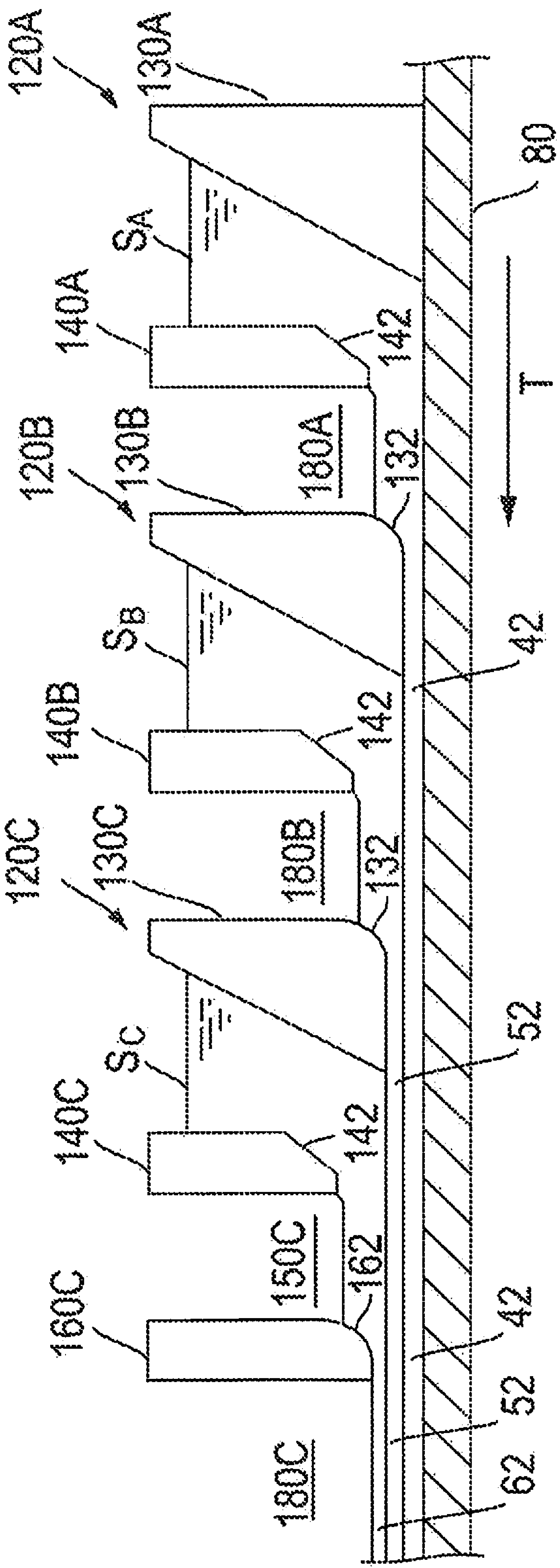
FIG. 21C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S_C
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142
150C
162
160C
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52
180C
62

FIG. 22

DIE HEAD APPARATUS, COATING METHOD, AND LAMINATED BODY FORMING APPARATUS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a U.S. national stage application of International Application No. PCT/JP2018/003198, filed on Jan. 31, 2018. The present application is based on Japan Patent Application No. 2017-048731 filed on Mar. 14, 2017, and the contents disclosed therein are incorporated herein as a whole by reference.

BACKGROUND

Technical Field

The present invention relates to a die head apparatus, a coating method, and a laminated body forming apparatus.

Background Art

For example, a die head apparatus that is used for application of a slurry is known (for example, refer to Japanese Laid-Open Patent Application No. 2003-10766.).

The slurry is prepared by dispersing a powdered material in a liquid medium, and contains impurities such as bubbles and dust. Therefore, there is the problem that bubble failure (impurity failure) may occur due to bubbles remaining on a coating film that is formed by application of the slurry, or that it may be difficult to form a coating film of uniform thickness. In particular, the problems described above are significant in a laminated body of coating films that are formed by repeated application of the slurry.

At the same time, a bubble removal device (dedicated device for removal of impurities) for removing the bubbles contained in the slurry is known (for example, refer to Japanese Laid-Open Patent Application No. 2011-50814.).

SUMMARY

Although it is possible to remove the bubbles contained in the slurry by using the bubble removal device before applying the slurry, this method has such problems as causing an increase in the size of the overall device, an increase in the cost of the device due to greater complexity of the device configuration, and a reduction in productivity due to an increase in the number of processes.

In order to solve the problem associated with the prior art described above, the object of the present invention is to provide a coating method and a die head apparatus that can form a coating film of uniform thickness without impurity failures and without a dedicated device for the removal of impurities, and a laminated body forming apparatus that can form a laminated body of the coating film.

One aspect of the present invention which achieves the object above is a die head apparatus for applying a slurry to a substrate that is transported to form a coating film, comprising a front blade, a rear blade, a center blade, and an internal impurity removal space. The front blade and the center blade are configured to form a slurry pool. The internal impurity removal space is positioned between the center blade and the rear blade. The distance separating the rear blade and the substrate is set smaller than the distance separating the center blade and the substrate.

Another aspect of the present invention which achieves the object above is a coating method for applying a slurry to a substrate that is transported to form a coating film. In the above-described coating method for forming the coating film with a uniform thickness: when the substrate passes the center blade, the slurry is applied to the substrate; when the substrate passes through the internal impurity removal space, the impurities contained in the coating film of the slurry that is applied to the substrate are removed by floating to the surface of the coating film and escaping therefrom; and when the substrate passes the rear blade, the surface of the coating film is smoothed.

Yet another aspect of the present invention which achieves the object above is a laminated body forming apparatus for forming a laminated body of a coating film on a transported substrate, comprising a plurality of the die head apparatuses, where the plurality of die head apparatuses are arranged in series along the substrate transport direction, and external impurity removal spaces for removing impurities that are contained in a coating film slurry are provided on downstream sides of the plurality of die head apparatuses in the transport direction.

By means of one aspect and another aspect of the present invention, since, after passing the center blade, the coating film slurry has small thickness, in the internal impurity removal space located between the center blade and the rear blade, the impurities contained in the coating film are removed by floating to the surface of the coating film and escaping. In addition, when the substrate passes the rear blade, the surface of the coating film is smoothed (corrected), thereby forming the coating film with uniform thickness. Thus, it is possible to provide a coating method and die head apparatus that can form a coating film of uniform thickness without impurity failures and without a dedicated device for the removal of impurities.

By means of yet another aspect of the present invention, in the coating film formed by the die head apparatus, the remaining impurities are removed in the external impurity removal space, after which another slurry is applied to the surface of the coating film by another die head apparatus, thereby forming a laminated body of the coating films. Thus, it is possible to provide a coating method and laminated body forming apparatus that can form a laminated body of the coating films of uniform thickness without impurity failures and without a dedicated device for the removal of impurities.

Other objects, features, and characteristics of the present invention should become apparent with reference to the preferred embodiments illustrated in the following descriptions and appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a cross-sectional view for explaining a half-cell layer of a fuel cell according to an embodiment of the present invention.

FIG. **2** is a side view for explaining a laminated body forming apparatus for forming the half-cell layer shown in FIG. **1**.

FIG. **3** is a schematic view for explaining the formation of a laminated body by the laminated body forming apparatus.

FIG. **4** is a perspective view for explaining a die head apparatus shown in FIG. **2**.

FIG. **5** is a perspective view for explaining an internal structure of the die head apparatus.

FIG. **6** is a cross-sectional view for explaining the internal structure of the die head apparatus.

FIG. **7** is a schematic view for explaining the formation of the coating film by the die head apparatus.

FIG. **8** is a flow chart for explaining a coating method according to an embodiment of the present invention.

FIG. **9** is a flow chart for explaining a first coating film forming step shown in FIG. **8**.

FIG. **10**A is a perspective view for explaining a first modified example according to the embodiment of the present invention.

FIG. **10**B is a bottom surface view for explaining the first modified example according to the embodiment of the present invention.

FIG. **11**A is a perspective view for explaining a second modified example according to the embodiment of the present invention.

FIG. **11**B is a bottom surface view for explaining the second modified example according to the embodiment of the present invention.

FIG. **12** is a cross-sectional view for explaining a third modified example according to the embodiment of the present invention.

FIG. **13** is a cross-sectional view for explaining a fourth modified example according to the embodiment of the present invention.

FIG. **14** is a cross-sectional view for explaining a fifth modified example according to the embodiment of the present invention.

FIG. **15** is a cross-sectional view for explaining a sixth modified example according to the embodiment of the present invention.

FIG. **16** is a cross-sectional view for explaining a seventh modified example according to the embodiment of the present invention.

FIG. **17** is a cross-sectional view for explaining an eighth modified example according to the embodiment of the present invention.

FIG. **18** is a cross-sectional view for explaining a ninth modified example according to the embodiment of the present invention.

FIG. **19** is a side view for explaining a tenth modified example according to the embodiment of the present invention.

FIG. **20** is a side view for explaining an eleventh modified example according to the embodiment of the present invention.

FIG. **21**A is a cross-sectional view for explaining the die head apparatus positioned on a most upstream side of a transport direction shown in FIG. **20**.

FIG. **21**B is a cross-sectional view for explaining the die head apparatus positioned downstream of the die head apparatus of FIG. **21**A in the transport direction.

FIG. **21**C is a cross-sectional view for explaining the die head apparatus positioned downstream of the die head apparatus of FIG. **21**B in the transport direction.

FIG. **22** is a schematic view for explaining the formation of the laminated body by the laminated body forming apparatus shown in FIG. **20**.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Embodiments of the present invention are described below with reference to the drawings. The dimensional ratios of the drawings are exaggerated for convenience of explanation and may differ from the actual ratios.

FIG. **1** is a cross-sectional view for explaining a half-cell layer of a fuel cell according to an embodiment of the present invention.

A fuel cell **10** according to the embodiment of the present invention is a solid oxide fuel cell (SOFC) having a cathode layer **20** and a half-cell layer **30**, as shown in FIG. **1**.

The cathode layer **20** is, for example, an air electrode layer having a thickness of 10-50 μm and is in contact with the half-cell layer **30**. The cathode layer **20** has catalytic ability and electronic conductivity and comprises a conductive ceramic, for example.

The half-cell layer **30** is a laminated body comprising three layers, including a metal support layer **40**, an anode layer **50**, and a solid electrolyte layer **60**.

The metal support layer **40** has a thickness of, for example, 100-800 μm. The metal support layer **40** is electronically conductive and has a function of supporting expansion and contraction of a battery. Specifically, the metal support layer **40** comprises a metal material, such as stainless steel.

The anode layer **50** is, for example, a fuel electrode layer having a thickness of 10-50 μm. The anode layer **50** has catalytic ability, electronic conductivity, and ionic conductivity. Specifically, the anode layer **50** contains an activation catalyst, a metal-based material, and a ceramic-based material.

The solid electrolyte layer **60** has, for example, a thickness of 1-30 μm, and is sandwiched by the cathode layer **20** and the anode layer **50**. The solid electrolyte layer **60** has ionic conductivity, and comprises, for example, a ceramic-based material, such as stabilized zirconia.

Next, a laminated body forming apparatus **100** for forming the half-cell layer will be described.

FIG. **2** is a side view for explaining the laminated body forming apparatus for forming the half-cell layer shown in FIG. **1**, and FIG. **3** is a schematic view for explaining the formation of the laminated body by means of the laminated body forming apparatus.

As shown in FIGS. **2** and **3**, the laminated body forming apparatus **100** is a roll-to-roll coating device that forms a laminated body of coating films **42**, **52**, **62** by applying three types of slurries S_A, S_B, S_C on a thin-film sheet-like substrate **80**. Reference symbols D_{4A}, D_{4B}, and D_{4C} indicate the thicknesses of the coating films **42**, **52**, **62**, and the reference symbol T indicates the transport direction of the substrate **80**. A case in which bubbles (air bubbles) are contained as impurities in the coating films **42**, **52**, **62** in the present embodiment will be described.

The material of the substrate **80** is not particularly limited. However, in the present embodiment, the formed laminated body of the coating films **42**, **52**, **62** is peeled off of the substrate **80**; thus, the material of the substrate **80** is preferably a resin having good releasability. Examples of resins having good releasability include polyethylene terephthalate (PET), polytetrafluoroethylene (PTFE), and silicone resin.

The laminated body forming apparatus **100** comprises a transport device **110**, die head apparatuses **120**A, **120**B, **120**C, slurry supply devices **170**A, **170**B, **170**C, external bubble removal spaces (external impurity removal spaces) **180**A, **180**B, **180**C, and a control device **190**.

As shown in FIG. **2**, the transport device **110** is used for transporting the substrate **80** and includes a feed roll **111**, a drive roller **112**, a take-up roll **114**, a tension control device **115**, and a support table **117**.

The feed roll **111**, around which the substrate **80** is wound in the form of a roll, is rotatably disposed. The drive roller **112** is used to feed the substrate **80** from the feed roll **111** and to supply the substrate to the die head apparatuses **120**A, **120**B, **120**C by means of friction force.

The drive roller **112** is configured to have a variable rotational speed so as to be capable of adjusting the transport speed of the substrate **80**. The drive roller **112** is, for example, a resin roller formed from a resin having good a coefficient of friction, a rubber roller formed from a rubber having a good coefficient of friction, or a metal roller having a coating layer of resin or rubber that has a good coefficient of friction.

The installed number and positions of the drive rollers **112** are appropriately set in consideration of the materials of the slurries, the installed number of the die head apparatuses, the transport distance, and the like. For example, the drive roller **112** can be disposed downstream of the die head apparatus **120**C in the transport direction T, or downstream of each of the die head apparatuses **120**A, **120**B, **120**C in the transport direction T.

The take-up roll **114** is rotatably disposed and is used to take up the substrate **80**, on which the laminated body of the coating films **42**, **52**, **62** is disposed, in the form of a roll. The tension control device **115** controls the tension of the substrate **80** by adjusting the rotational speed of the take-up roll **114** and is configured to suppress, for example, the formation of wrinkles in the substrate **80**, the stretching of the substrate **80**, and the breakage of the substrate **80**.

The support table **117** supports the back surface of the substrate **80** to be transported, and the contact surface with the substrate **80** has a good degree of smoothness in order to ensure the smooth transport of the substrate **80**. From the standpoint of precise flatness, the support table **117** is preferably formed from a glass plate, a stone surface plate, or a stainless-steel plate, but no limitation is imposed thereby. For example, the material of the support table **117** is appropriately selected in consideration of cost and weight, in addition to precise flatness.

The die head apparatuses **120**A, **120**B, **120**C are disposed in series and adjacent to each other in the transport direction T of the substrate **80** (refer to FIG. **3**). The die head apparatus **120**A is configured to form the coating film **42** which constitutes the metal support layer **40** of the half-cell layer **30**. The die head apparatus **120**B is configured to form the coating film **52** which constitutes the anode layer **50** of the half-cell layer **30**. The die head apparatus **120**C is configured to form the coating film **62** which constitutes the solid electrolyte layer **60** of the half-cell layer **30**.

The slurry supply devices **170**A, **170**B, **170**C include slurry tanks **172**A, **172**B, **172**C, pumps **174**A, **174**B, **174**C, and piping systems **176**A, **176**B, **176**C.

The slurry tanks **172**A, **172**B, **172**C accommodate slurries S_A, S_B, S_C that form the coating films **42**, **52**, **62**. The viscosity of the slurries S_A, S_B, S_C is, for example, 5,000-50,000 cP. The pumps **174**A, **174**B, **174**C are gear pumps, such as mono pumps or Viking pumps, or are screw pumps, and are used to feed the slurries S_A, S_B, S_C.

The slurry S_A contains powder of the material that constitutes the metal support layer **40**. The slurry S_B contains powder of the material that constitutes the anode layer **50**. The slurry S_C contains powder of the material that constitutes the solid electrolyte layer **60**. In addition to the above, the slurries S_A, S_B, S_C appropriately contain a dispersion medium, an additive, and the like. The dispersion medium is, for example, an alcohol solvent, an ether solvent, an ester solvent, a ketone solvent, a cyclic ether solvent, or an aromatic hydrocarbon solvent. The additive is, for example, a sintering aid or a thickener.

The piping systems **176**A, **176**B, **176**C connect the slurry tanks **172**A, **172**B, **172**C, the pumps **174**A, **174**B, **174**C, and the die head apparatuses **120**A, **120**B, **120**C, and also include filters **177**A, **177**B, **177**C and pressure gauges **178**A, **178**B, **178**C.

The filters **177**A, **177**B, **177**C are configured to remove large dust, aggregates, etc., contained in the slurries S_A, S_B, S_C. The pressure gauges **178**A, **178**B, **178**C are used to detect the supply pressure of the slurries S_A, S_B, S_C.

The external bubble removal spaces **180**A, **180**B, **180**C are provided downstream of the die head apparatuses **120**A, **120**B, **120**C, respectively, in the transport direction T and are configured to remove bubbles (impurities) contained in the coating films **42**, **52**, **62** (refer to FIG. **3**). The external bubble removal spaces **180**A, **180**B, **180**C also have the function of securing the time required for leveling, drying, and curing the coating films **42**, **52**, **62** and facilitating the stacking. Accordingly, since the occurrence of mixing (mixing) at the interfaces of the coating films **42**, **52**, **62** is suppressed, there is excellent flexibility in the applicable slurry types.

The control device **190** comprises a control circuit having a microprocessor, and the like, which execute various controls and calculation processes in accordance with a program. The control device **190** is connected to the drive roller **112**, the tension control device **115**, the slurry tanks **172**A, **172**B, **172**C, and the pumps **174**A, **174**B, **174**C, and various functions of the laminated body forming apparatus **100** are realized by means of execution of the corresponding programs by the control device **190**.

The slurry supply device is not limited to the configuration described above; it is also possible to apply, for example, a dispenser that is capable of discharging the slurry. The dispenser capable of discharging the slurry is, for example, a dispenser manufactured by HEISHIN Ltd., in which is incorporated a structure similar to a mono pump.

Next, the die head apparatus is described in detail.

FIG. **4** is a perspective view for explaining the die head apparatus shown in FIG. **2**; FIGS. **5** and **6** are a perspective view and a cross-sectional view, respectively, for explaining an internal structure of the die head apparatus; and FIG. **7** is a schematic view for explaining the formation of the coating film by the die head apparatus.

As shown in FIGS. **4-6**, the die head apparatus **120**A comprises a casing **122**A, a supply part **124**A, a front blade **130**A, a center blade **140**A, an internal bubble removal space (internal impurity removal space) **150**A, a rear blade **160**A, an adjustment screws **137**A, **147**A, **167**A, and fixing screws **138**A, **148**A, **168**A.

The casing **122**A is essentially rectangular and has a bottom surface that faces the transported substrate **80** and an upper surface positioned on the opposite side of said bottom surface. An opening for applying the slurry S_A to the substrate **80** is formed on the bottom surface of the casing **122**A. The supply part **124**A is disposed on the upper surface of the casing **122**A.

The supply part **124**A has a slit **125**, to which the piping system **176**A of the slurry supply device **170**A is connected. The slit **125** is disposed at the outlet of the supply part **124**A and is configured to evenly supply the slurry S_A in a lateral direction L orthogonal to the transport direction T (refer to FIG. **5**). The slit **125** can be appropriately omitted as deemed necessary.

The supply width of the slurry S_A corresponds to the length of the slit **125** along the lateral direction L orthogonal to the transport direction T. The supply thickness of the slurry S_A corresponds to the width of the slit **125** in the transport direction T.

The front blade **130**A has a right triangular cross section and extends in the lateral direction L (refer to FIGS. **5** and **6**). The front blade **130**A has a front surface **131** positioned on the upstream side in the transport direction T and a back surface **134** positioned on the downstream side in the transport direction T. The front surface **131** extends in a vertical direction V with respect to the transport direction T. The back surface **134** has an inclined surface **135** that corresponds to the hypotenuse of a right triangle. The inclined surface **135** is positioned immediately below the slit **125** and is configured such that the slurry S_A flows downward toward the center blade **140**A. The angle of inclination of the back surface **134** is appropriately set in consideration of the viscosity of the slurry S_A, and the like.

The adjustment screw **137**A is connected to the upper portion of the front blade **130**A and is configured to be capable of moving the front blade **130**A along the vertical direction V. Accordingly, it is possible to change the distance separating the front blade **130**A and the substrate **80** by adjusting the adjustment screw **137**A. For example, the distance separating the front blade **130**A from the substrate **80** is set so that there is no interference with the passage of the substrate **80** and so that the slurry S_A does not flow out.

The fixing screw **138**A is positioned to face a side surface of the front blade **130**A. The fixing screw **138**A is configured to fix the position of the front blade **130**A, which is adjusted by the adjustment screw **137**A, by abutting the side surface of the front blade **130**A.

The center blade **140**A is positioned downstream of the front blade **130**A in the transport direction T, has an essentially rectangular cross section, and extends in the lateral direction L (refer to FIGS. **5** and **6**). The center blade **140**A has a front surface **141** positioned on the upstream side in the transport direction T and a back surface **144** positioned on the downstream side in the transport direction T. The front surface **141** faces the back surface **134** of the front blade **130**A and has an irregularly shaped portion **142**. The center blade **140**A is configured to form a pool of the slurry S_A together with the front blade **130**A.

The adjustment screw **147**A is connected to the upper portion of the center blade **140**A and is configured to be capable of moving the center blade **140**A in the vertical direction V. Thus, it is possible to change the distance separating the center blade **140**A and the substrate **80** by adjusting the adjustment screw **147**A.

The fixing screw **148**A is positioned to face a side surface of the center blade **140**A. The fixing screw **148**A is configured to fix the position of the center blade **140**A, which is adjusted by the adjustment screw **147**A, by abutting the side surface of the center blade **140**A.

Since the slurry S_A has a high viscosity (for example, 5,000-50,000 cP) and the liquid pressure is high inside the slurry S_A pool, the bubbles contained in the slurry S_A do not readily rise. In addition, because there is normally a high pressure loss, bubbles remain in the gap between the center blade **140**A and the substrate **80** and gather to form large bubbles. Therefore, there is the risk that bubble failure (impurity failure) occurs in the coating film that is formed by passing the center blade **140**A.

However, the irregularly shaped portion **142** of the front surface **141** of the center blade **140**A comprises a sloped portion that is inclined in the transport direction T and functions as a rotation application portion that applies a rotational force to the slurry S_A in the pool (refer to FIG. **7**). Therefore, the bubbles contained in the slurry S_A do not remain there, and are efficiently fed to the back surface **144** of the center blade **140**A without aggregating to form large bubbles, so that the occurrence of bubble failure is suppressed.

The angle of inclination θ of the irregularly shaped portion (sloped portion) **142**, although dependent on the viscosity of the slurry S_A, is preferably 30-60°. The angle of inclination θ of the irregularly shaped portion (sloped portion) **142** preferably does not vary with respect to the lateral direction L. Variation in the width W_1 of the distal end portion of the center blade **140**A is preferably suppressed within the range of 0.003-0.1 mm, in absolute value. The width W_1, although dependent on the viscosity of the slurry S_A, can be set to 0 mm, that is, to an acute angle.

The rotational force of the slurry S_A is not limited to being controlled by use of the angle of inclination θ and may be controlled by use of, for example, the pressure at which the slurry S_A passes the center blade **140**A (passage pressure). The passage pressure can be adjusted by increasing the transport speed of the substrate **80** or pressurizing the slurry S_A in the pool.

The rear blade **160**A is positioned downstream of the center blade **140**A in the transport direction T, has an essentially rectangular cross section, and extends in the lateral direction L (refer to FIGS. **5** and **6**). The rear blade **160**A has a front surface **161** positioned on the upstream side in the transport direction T and a back surface **164** positioned on the downstream side in the transport direction T. The front surface **161** faces the back surface **144** of the center blade **140**A and has an irregularly shaped portion **162**.

The adjustment screw **167**A is connected to the upper portion of the rear blade **160**A and is configured to be capable of moving the rear blade **160**A along the vertical direction V. Accordingly, it is possible to change the distance separating the rear blade **160**A and the substrate **80** by adjusting the adjustment screw **167**A.

The fixing screw **168**A is positioned to face a side surface of the rear blade **160**A. The fixing screw **168**A is configured to fix the position of the rear blade **160**A, which is adjusted by the adjustment screw **167**A, by abutting the side surface of the rear blade **160**A.

The distance D_{2A} separating the rear blade **160**A and the substrate **80** is set smaller than the distance D_{1A} separating the center blade **140**A and the substrate **80** (refer to FIG. **7**). Accordingly, the surface of the coating film of the slurry S_A is smoothed (corrected) when the substrate passes the rear blade **160**A by using an ironing effect of the press, thereby forming the coating film **42** with a uniform thickness.

The irregularly shaped portion **162** comprises a quarter-circle (fan-shaped) curved portion. The distance D_{3A} separating the substrate **80** and the start position SP of the irregularly shaped portion (curved portion) **162** is set larger than the distance D_{1A} separating the center blade **140**A and the substrate **80**. Accordingly, the irregularly shaped portion (curved portion) **162** functions as a guide portion that guides the bubbles contained in the coating film to the surface of the coating film to thereby efficiently remove the air bubbles contained in the coating film.

The variation in the width W_2 of the distal end portion of the rear blade **160**A at the end position EP of the irregularly shaped portion (curved portion) **162** is preferably suppressed within the range of 0.003-0.1 mm, in absolute value. The width W_2, although dependent on the viscosity of the slurry S_A, can be set to 0 mm, that is, to an acute angle.

The internal bubble removal space **150**A is positioned between the center blade **140**A and the rear blade **160**A and is provided in order to remove bubbles (impurities) contained in the coating film of the slurry S_A, which are applied to the substrate **80** (refer to FIGS. **6** and **7**).

That is, after the slurry S_A passing the center blade **140**A, the slurry S_A has a small thickness and the liquid pressure is decreased, so that the bubbles readily rise. In addition, there is also the effect that, when the dispersion medium in the slurry evaporates, air bubbles are entrained to the surface. Accordingly, in the internal bubble removal space **150**A, the bubbles are easily removed by floating to the surface of the coating film and escaping. The depressions on the surface created by the bubbles escaping are pressed when passing the rear blade **160**A and smoothed, thereby ensuring that the coating film **42** has a uniform thickness.

The materials of the front blade **130**A, the center blade **140**A, and the rear blade **160**A are preferably 400 series stainless steel, 600 series stainless steel, cemented carbide, or the like from the standpoint of precise flatness and parallelism. At least the surfaces of the front blade **130**A, the center blade **140**A, and the rear blade **160**A that come into contact with the slurry S_A are preferably lapped in order to prevent inhibition of the flowability of the slurry S_A and contamination due to aggregation.

The die head apparatuses **120**B, **120**C have essentially the same configuration as the die head apparatus **120**A; thus, similar reference symbols have been assigned to members having similar functions, and the descriptions thereof have been omitted to avoid redundancy.

Since the substrate **80** on which the coating film has been formed is supplied to the die head apparatuses **120**B, **120**C, the respective distances separating the front blades **130**B, **130**C, the center blades **140**B, **140**C, and the rear blades **160**B, **160**C from the substrate **80** are appropriately set in consideration of the thicknesses D_{4A}, D_{4B} of the coating film (refer to FIG. **3**).

For example, the distance separating the front blade **130**B of the die head apparatus **120**B from the substrate **80** is set so that there is no interference with the passage of the substrate **80** on which the coating film **42** with the thickness D_{4A} is formed, and so that the slurry S_B does not flow out. The distance separating the front blade **130**C of the die head apparatus **120**C from the substrate **80** is set so that there is no interference with the passage of the substrate **80** on which the coating film **42** with the thickness D_{4A} and the coating film **52** with the thickness D_{4C} are formed, and so that the slurry S_C does not flow out.

As described above, by using the die head apparatus according to the present embodiment, it is possible to form the coating film of uniform thickness without bubble failures (impurity failures) and without using a dedicated bubble removal device (for the removal of impurities). In addition, by using the laminated body forming apparatus according to the present embodiment, in the coating film formed by the die head apparatus, the remaining impurities are removed in the external impurity removal space, after which another slurry is applied to the surface thereof by another die head apparatus, thereby forming a laminated body of the coating film. Accordingly, it is possible to form the laminated body of the coating film of uniform thickness without bubble failures (impurity failures) and without using a dedicated bubble removal device (for removal of impurities).

The number of die head apparatuses provided in the laminated body forming apparatus is not limited to three and is appropriately set in accordance with, for example, the configuration of the laminated body to be formed. In addition, a single die head apparatus may be used by itself.

From the standpoint of suppressing unexpected contamination and admixtures of foreign objects in the coating film, the laminated body forming apparatus is preferably installed in a cleanroom.

The laminated body forming apparatus is not limited to the roll-to-roll system, and a roll-to-sheet system may be applied as well.

The laminated body forming apparatus and the die head apparatus are not limited to a mode that is applied to forming the half-cell layer of the solid oxide fuel cell (SOFC) and may be applied to the formation of layers that constitute a lithium-ion battery or a polymer electrolyte membrane fuel cell (PEM-FC).

For example, in the case of application to a lithium-ion battery, the substrate is the current collector made from a metal film such as copper foil, aluminum foil, or stainless steel foil, and the slurry contains a powder of a material constituting the active material layer. In the case of application to a polymer electrolyte membrane fuel cell, the substrate is the electrolyte membrane, and the slurry contains a powder of a material constituting the catalyst layer. Alternatively, the substrate is a resin sheet (auxiliary material) made of a PTFE sheet or a PET sheet, the slurry contains a powder of a material constituting the catalyst layer and is attached to a separately formed electrolyte membrane. The resin sheet is peeled off of the catalyst layer at an appropriate timing.

The coating method to which the laminated body forming apparatus **100** is applied will now be described.

FIG. **8** is a flow chart for explaining the coating method according to an embodiment of the present invention. The functions corresponding to the steps of the flow chart shown in FIG. **8** are realized by using execution of the corresponding programs by the control device **190**.

The coating method according to the embodiment of the present invention is used for coating three types of the slurries S_A, S_B, S_C on the thin film sheet-like substrate **80** to form the laminated body of the coating films **42**, **52**, **62**, and, as shown in FIG. **8**, comprises a first coating film formation step, a first external bubble removal step (first external impurity removal step), a second coating film formation step, a second external bubble removal step (second external impurity removal step), a third coating film formation step, and a third external bubble removal step (third external impurity removal step).

In the first coating film formation step, the slurry S_A is supplied from the slurry supply device **170**A to the die head apparatus **120**A, and the coating film **42** with the thickness D_{4A} is formed on the substrate **80** (refer to FIG. **3**). The slurry S_A contains a powder of a material constituting the metal support layer **40** of the half-cell layer **30**, and thus the coating film **42** constitutes the metal support layer **40**.

The substrate **80**, wound in a roll around the feed roll **111** and fed from the feed roll **111** by means of the friction force of the drive roller **112**, is continuously transported toward the take-up roll **114** via the die head apparatus **120**A, the external bubble removal space **180**A, the die head apparatus **120**B, the external bubble removal space **180**B, the die head apparatus **120**C, and the external bubble removal space **180**C.

In the first external bubble removal step, the bubbles contained in the coating film **42** are removed when the substrate **80** on which the coating film **42** is formed passes through the external bubble removal space **180**A provided downstream of the die head apparatus **120**A in the transport direction T.

In the second coating film formation step, the slurry S_B is supplied from the slurry supply device **170**B to the die head apparatus **120**B, and the coating film **52** with the thickness D_{4B} is formed on the substrate **80**. The slurry S_B contains a powder of a material constituting the anode layer **50** of the half-cell layer **30**, and thus the coating film **52** constitutes the anode layer **50**.

In the second external bubble removal step, the bubbles contained in the coating film **52** are removed when the substrate **80** on which the coating films **42**, **52** are formed passes through the external bubble removal space **180**B provided downstream of the die head apparatus **120**B in the transport direction T.

In the third coating film formation step, the slurry S_C is supplied from the slurry supply device **170**C to the die head apparatus **120**C, and the coating film **62** with the thickness D_{4C} is formed on the substrate **80**. The slurry S_C contains a powder of a material constituting the solid electrolyte layer **60** of the half-cell layer **30**, and thus the coating film **62** constitutes the solid electrolyte layer **60**.

In the third external bubble removal step, the bubbles contained in the coating film **62** is removed when the substrate **80** on which the coating films **42**, **52**, **62** are formed passes through the external bubble removal space **180**C provided downstream of the die head apparatus **120**C in the transport direction T. The substrate **80** on which the coating films **42 52**, **62** are formed is then wound in a roll around the take-up roll **114**.

After being peeled off of the substrate **80**, the laminated body of the coating films **42**, **52**, **62** is subjected to, for example, a degreasing step and a firing step to become the half-cell layer **30** comprising the metal support layer **40**, the anode layer **50**, and the solid electrolyte layer **60**.

The first coating film forming step to which the die head apparatus **120**A is applied will now be described in detail.

FIG. **9** is a flow chart for explaining a first coating film formation step shown in FIG. **8**.

The substrate **80** that is fed from the feed roll **111** passes the front blade **130**A (refer to FIG. **7**).

The substrate **80** then passes through the pool of the slurry S_A formed between the front blade **130**A and the center blade **140**A, and, thus applying the slurry S_A with the center blade **140**A and forming the coating film.

At this time, the irregularly shaped portion (sloped portion) **142** of the center blade **140**A functions as a rotation application part that applies a rotary force to the slurry S_A, and the bubbles contained in the slurry S_A do not remain and are efficiently fed to the back surface **144** of the center blade **140**A without aggregating to form large bubbles.

The substrate **80** then passes through the internal bubble removal space **150**A. At this time, since the thickness of the coating film formed on the substrate **80** is thin, the bubbles contained in the coating film are removed when the bubbles float to the surface of the coating film and escape.

The substrate **80** then passes by the rear blade **160**A. At this time, since the distance D_{2A} separating the rear blade **160**A and the substrate **80** is set smaller than the distance D_{1A} separating the center blade **140**A and the substrate **80**, the surface of the coating film formed on the substrate **80** is smoothed (corrected) by means of the ironing effect of the press; in this way, the coating film **42** is formed with uniform thickness.

In addition, the distance D_{3A} separating the substrate **80** and the start position SP of the irregularly shaped portion (curved portion) **162** of the rear blade **160**A is set larger than the distance D_{1A} separating the center blade **140**A and the substrate **80**. Accordingly, the irregularly shaped portion (curved portion) **162** functions as a guide portion that guides the bubbles contained in the coating film to the surface of the coating film to thereby efficiently remove the air bubbles contained in the coating film. Thereafter, the substrate **80** is transported to the first external bubble removal step (external bubble removal space **180**A).

As described above, by means of the coating method according to the first coating film forming step, it is possible to form the coating film **42** with uniform thickness without bubble failures (impurity failures) and without using a dedicated bubble removal device (for the removal of impurities).

The operations of the second and third coating film forming steps to which the die head apparatuses **120**B, **120**C are applied have essentially the same configuration as the operation of the first coating film forming step to which the die head apparatus **120**A is applied, so that the descriptions thereof are omitted.

Next, a performance evaluation of examples produced by means of the coating method according to the present embodiment will be described.

In the performance evaluation, the thicknesses of the solid electrolyte layers and the anode layers were compared in terms of uniformity. The uniformity of thickness was evaluated by examining the variation in thickness of each layer. The bubble removal effect was compared for the metal support layers. The bubble removal effect was evaluated based on the bubble generation rate. Comparative examples were formed using a film applicator (doctor blade) manufactured by Yasuda Seiki Seisakusho. In the formation of the metal support layers in the comparative example, the slurry constituting the metal support layer was applied in a state in which bubbles were contained in the slurry and was not subjected to preliminary bubble removal.

The absolute value of the variation in the thicknesses of the solid electrolyte layers was 5 μm for the examples and 21 μm for the comparative examples. The absolute value of the variation in the thicknesses of the anode layers was 3 μm for the examples and 25 μm for the comparative examples. The bubble generation rate per 100 mm^2 of the metal support layer was 10 for the examples and greater than or equal to 200 for the comparative example.

As described above, unlike the comparative examples, the examples had a good uniformity of thickness and a low bubble generation rate.

Next, first and second modified examples are described.

In the following FIGS. **10**A to **18**, the casing, the front blades, the center blades, the internal bubble removal spaces, and the rear blades of the die head apparatuses **120**A, **120**B, **120**C are respectively designated by reference numerals **122**, **130**, **140**, **150**, and **160**. The slurries S_A, S_B, S_C are designated by the reference symbol S. In addition, the distances separating the front blade **130**, the center blade **140**, and the rear blade **160** from the substrate **80** are represented by the setting of the die head apparatus **120**A.

FIGS. **10**A and **10**B are a perspective view and a bottom surface view for explaining the first modified example according to the embodiment of the present invention, and FIGS. **11**A and **11**B are a perspective view and a bottom surface view for explaining the second modified example according to the embodiment of the present invention.

The angle of inclination of the irregularly shaped portion **142** of the center blade **140** preferably is constant with respect to the transport direction T and the vertical direction V when the slurry is constantly fed in a state of evenly spreading out in the lateral direction. However, there are cases in which turbulent flow occurs in the slurry in the slurry pool that is formed between the center blade **140** and the front blade. In this case, it is preferable to laminarize the flow of the slurry by changing the width of the distal end portion of the center blade **140** and the angle of inclination of the irregularly shaped portion **142** in the lateral direction L.

For example, when the slurry supply part **124** is disposed above the central portion of the slurry pool and the flow of the slurry from the central portion to the two ends occurs in the slurry pool, as shown in FIGS. **10**A and **10**B, it is preferable to laminarize the flow of the slurry by making the width of the distal end portion of the central portion **146**B of the center blade **140** in the lateral direction L thicker than the width of the distal end portions on the both ends **146**A, **146**C.

In addition, for example, when the slurry supply part **124** is disposed above one end of the slurry pool and the flow of the slurry from the one end to the other end occurs in the slurry pool, as shown in FIGS. **11**A and **11**B, it is preferable to laminarize the flow of the slurry by making the width of the distal end portion of the one end **146**A of the center blade **140** in the lateral direction L thicker than the width of the distal end portions of the other end **146**C.

Next, third and fourth modified examples are described.

FIGS. **12** and **13** are cross-sectional views for explaining the third and fourth modified examples according to the embodiment of the present invention.

The irregularly shaped portion **142** of the center blade **140** constituting the rotation application portion that applies a rotational force to the slurry S is not limited to being configured by the sloped portion. For example, the irregularly shaped portion **142** can also be configured from the curved portion shown in FIG. **12**, or from a shape that has both the curved portion **143**B and the inclined portion **143**A shown in FIG. **13**.

Next, a fifth modified example is described.

FIG. **14** is a cross-sectional view for explaining the fifth modified example according to the embodiment of the present invention.

The center blade **140** preferably has a guide portion **145** on the back surface **144** of the distal end portion. The guide portion **145** comprises, for example, the inclined portion shown in FIG. **14**, and is configured to guide the coating film of the slurry S away from the substrate **80** and toward the internal bubble removal space **150**. In this case, the slurry S is discharged so as to be guided by the guide portion **145** and expand, so that efficient removal of the air bubbles contained in the slurry S is possible.

Next, sixth to eighth modified examples are described.

FIGS. **15-17** are cross-sectional views for explaining the sixth to the eighth modified examples according to the embodiment of the present invention.

The irregularly shaped portion **162** of the rear blade **160** constituting the guide portion that guides the bubbles contained in the coating film of the slurry S to the surface of the coating film is not limited to being comprised of the quarter-circle (fan-shaped) curved portion. For example, the irregularly shaped portion **162** can also be configured from the inclined portion shown in FIG. **15**, configured from a shape that has both the curved portion **163**B and the inclined portion **163**A shown in FIG. **16**, or be configured from the roller-shaped curved portion shown in FIG. **17**. If the irregularly shaped portion **162** is configured by the roller-shaped curved portion, it is possible to reliably smooth (correct) the surface of the coating film.

Next, a ninth modified example is described.

FIG. **18** is a cross-sectional view for explaining the ninth modified example according to the embodiment of the present invention.

The internal bubble removal space **150** is not limited to the mode of being under atmospheric pressure (open system), and may be under negative pressure. In this case, since it becomes easy for the bubbles contained in the coating film of the slurry to float to the surface, the bubbles are reliably removed.

The negative pressure of the internal bubble removal space **150** can be achieved by, for example, disposing a hollow vessel **154** and a vacuum pump **152** in the die head apparatus, as shown in FIG. **18**.

The hollow vessel **154** has an opening **156** at the bottom and is disposed in the internal bubble removal space **150** positioned between the center blade **140** and the rear blade **160**. The opening **156** is positioned to face the substrate **80** that has passed the center blade **140**.

The vacuum pump **152** is connected to the hollow vessel **154** and is configured to be capable of placing the inside of the hollow vessel **154** at negative pressure by drawing the air from the interior of the hollow vessel **154**. In order to facilitate the generation of the negative pressure, the distance separating the opening **156** of the hollow vessel **154** and the substrate **80** on which the coating film is formed is preferably small.

Next, a tenth modified example is described.

FIG. **19** is a side view for explaining the tenth modified example according to the embodiment of the present invention.

As shown in FIG. **19**, the laminated body forming apparatus **100** can further comprise temperature control devices **182**A, **182**B, **182**C for promoting the drying of the coating film.

The temperature control devices **182**A, **182**B, **182**C include a hot air generator, an infrared irradiation device, and the like, are disposed in the external bubble removal spaces **180**A, **180**B, **180**C and are configured to be capable of drying the coating film by increasing the temperature of the coating film.

The temperature control devices **182**A, **182**B, **182**C are not limited to being disposed in the external bubble removal spaces **180**A, **180**B, **180**C and may be disposed on the lower side (back surface side) of the substrate **80**. In addition, the temperature control devices **182**A, **182**B, **182**C are not limited to being independent and may be integrated (incorporated) with the die head apparatuses **120**A, **120**B, **120**C.

Next, an eleventh modified example is described.

FIG. **20** is a side view for explaining the eleventh modified example according to the embodiment of the present invention; FIGS. **21**A, **21**B, and **21**C are cross-sectional views for explaining each of the die head apparatuses shown in FIG. **20**; and FIG. **22** is a schematic view for explaining the formation of the laminated body by the laminated body forming apparatus shown in FIG. **20**.

The laminated body forming apparatus **100** shown in FIG. **20** includes die head apparatuses **120**A, **120**B, **120**C having different configurations, and the device configuration is simplified compared to the laminated body forming apparatus **100** shown in FIG. **2**.

As shown in FIG. **21**A, the die head apparatus **120**A positioned on the farthest upstream side in the transport direction T does not have the internal bubble removal space **150**A and the rear blade **160**A.

As shown in FIG. **21**B, the die head apparatus **120**B positioned downstream of the die head apparatus **120**A in the transport direction T does not have the internal bubble removal space **150**B and the rear blade **160**B and has an irregularly shaped portion **132** on the front surface **131** of the front blade **130**B. The distance separating the front blade **130**B and the substrate **80** is set smaller than the distance separating the center blade **140**A of the die head apparatus **120**A and the substrate **80**, and the irregularly shaped portion **132** corresponds to the irregularly shaped portion **162** of the rear blade **160**A, which is omitted in the die head apparatus **120**A.

As shown in FIG. **21**C, the die head apparatus **120**C positioned downstream of the die head apparatus **120**B in the transport direction T has an irregularly shaped portion **132** on the front surface **131** of the front blade **130**C. The distance separating the front blade **130**C and the substrate **80** is set smaller than the distance separating the center blade **140**B of the die head apparatus **120**B and the substrate **80**, and the irregularly shaped portion **132** corresponds to the irregularly shaped portion **162** of the rear blade **160**B, which is omitted in the die head apparatus **120**B.

That is, the front blade **130**B of the die head apparatus **120**B, the external bubble removal space **180**A, the front blade **130**C of the die head apparatus **120**C, and the external bubble removal space **180**B also serve respectively as the rear blade **160**A of the die head apparatus **120**A, the internal bubble removal space **150**A of the die head apparatus **120**A, the rear blade **160**B of the die head apparatus **120**B, and the internal bubble removal space **150**B of the die head apparatus **120**B.

Specifically, as shown in FIG. **22**, the substrate **80** passes through the pool of the slurry S_A and the center blade **140**A, thus, applying the slurry S_A and forming the coating film.

The substrate **80** then passes through the external bubble removal space **180**A. At this time, since the thickness of the coating film of the slurry S_A is thin, the bubbles contained in the coating film are removed by floating to the surface of the coating film and escaping.

The substrate **80** then passes by the front blade **130**B of the die head apparatus **120**B. At this time, the surface of the coating film of the slurry S_A is smoothed (corrected) by means of the ironing effect of the press, thereby forming the coating film **42** with a uniform thickness. Additionally, the irregularly shaped portion (curved portion) **132** of the front blade **130**B functions as a guide portion that guides the bubbles contained in the coating film to the surface of the coating film to thereby efficiently remove the bubbles contained in the coating film **42**.

The substrate **80** then passes through the pool of the slurry S_B and the center blade **140**B, thus applying the slurry S_B and forming the coating film.

The substrate **80** then passes through the external bubble removal space **180**B. At this time, since the thickness of the coating film of the slurry S_B is thin, the bubbles contained in the coating film are removed by floating to the surface of the coating film and escaping.

The substrate **80** then passes by the front blade **130**C of the die head apparatus **120**C. At this time, the surface of the coating film is smoothed (corrected) by means of the ironing effect of the press, thereby forming the coating film **52** with a uniform thickness. Additionally, the irregularly shaped portion (curved portion) **132** of the front blade **130**C functions as a guide portion that guides the bubbles contained in the coating film to the surface of the coating film, thereby effecting the efficient removal of the bubbles contained in the coating film.

The substrate **80** then passes through the pool of the slurry S_C and the center blade **140**C, thus, applying the slurry S_C and forming the coating film.

Thereafter, the substrate **80** passes through the internal bubble removal space **150**C. At this time, since the thickness of the coating film of the slurry S_C is thin, the bubbles contained in the coating film are removed by floating to the surface of the coating film and escaping.

The substrate **80** then passes by the rear blade **160**C. At this time, the surface of the coating film is smoothed (corrected) by use of the ironing effect of the press, thereby forming the coating film **62** with uniform thickness. Additionally, the irregularly shaped portion (curved portion) **162** of the front blade **160**C functions as a guide portion that guides the bubbles contained in the coating film to the surface of the coating film to thereby efficiently remove the bubbles contained in the coating film. The substrate **80** then passes through the external bubble removal space **180**C.

As described above, by use of the die head apparatus and the coating method according to the present embodiment, since the thickness of the slurry is thin after passing by the center blade, in the internal bubble removal space (internal impurity removal space) positioned between the center blade and the rear blade, the bubbles (impurities) contained in the coating film of the slurry are removed by floating to the surface of the coating film and escaping. In addition, the slurry surface is smoothed (corrected) when the substrate passes by the rear blade, thereby forming the coating film with a uniform thickness. Accordingly, it is possible to provide a coating method and die head apparatus that can form a coating film of uniform thickness without bubble failures (impurity failures) and without using a dedicated bubble removal device (for the removal of impurities).

In the laminated body forming apparatus according to the present embodiment, the incorporated die head apparatus is able to form the coating film with uniform thickness without bubble failures and without using a dedicated device for bubble removal. In addition, in the coating film formed by the die head apparatus, the remaining bubbles are removed in the external bubble removal space (external impurity removal space), after which another slurry is applied to the surface thereof by another die head apparatus, thereby forming the laminated body of the coating film. Accordingly, it is possible to provide the laminated body forming apparatus that can form the laminated body of the coating film of uniform thickness without bubble failures and without using a dedicated device for bubble removal.

The center blade preferably has a rotation application portion that applies a rotational force to the slurry of the pool. In this case, it is possible to efficiently feed the bubbles contained in the coating film of the slurry to the internal bubble removal space.

The rotation application portion can be configured from an irregularly shaped portion having an inclined portion and/or a curved portion. In this case, the rotation application portion is embodied in a simple configuration.

The center blade preferably has a guide portion that guides the slurry in a direction away from the substrate and toward the internal bubble removal space. In this case, the slurry S is discharged so as to be guided by the guide portion and expand, so that efficient removal of the air bubbles contained in the slurry is possible.

The guide portion can be configured from an inclined portion. In this case, the guide portion of the center blade is embodied in a simple configuration.

The rear blade preferably has a guide portion that guides the bubbles contained in the coating film of the slurry to the surface of the coating film. In this case, it is possible to efficiently remove the air bubbles contained in the slurry.

The guide portion of the rear blade can be configured from an irregularly shaped portion having an inclined portion and/or a curved portion. In this case, the guide portion of the rear blade is embodied in a simple configuration.

The curved portion preferably has a roller shape. In this case, it is possible to reliably smooth (correct) the surface of the coating film.

The internal bubble removal space is preferably at negative pressure. In this case, since the bubbles contained in the coating film of the slurry readily float to the surface, the bubbles can be reliably removed.

In the laminated body forming apparatus, it is possible to simplify the device configuration by configuring the internal bubble removal space and the rear blade of the die head apparatus (first die head apparatus) to also serve as the external bubble removal space positioned on the downstream side in the transport direction and the front blade of the die head apparatus (second die head apparatus).

The front blade of the second die head apparatus preferably has a guide portion that guides the air bubbles remaining in the coating film to the surface of the coating film. In this case, it is possible to efficiently remove the air bubbles that remain in the coating film even after having passed through the external bubble removal space by use of the front blade of the second die head apparatus.

The guide portion of the front blade can be configured from an irregularly shaped portion having an inclined portion and/or a curved portion. In this case, the guide portion of the front blade is embodied in a simple configuration.

The present invention is not limited to the embodiment described above, and various modifications are possible within the scope of the claims. For example, the impurities to be removed is not limited to bubbles (air bubbles), and the present invention may also be applied to dust removal. In addition, it is possible to appropriately combine modified examples 1 to 11.

The invention claimed is:

1. A die head apparatus for forming a coating film by applying a slurry to a substrate that is transported, the die head apparatus comprising:
- a front blade that is positioned to abut a flat surface of the substrate from a direction above the substrate, the substrate extending along a horizontal direction that is orthogonal to a vertical length of the front blade that extends in a direction of gravity;
- a rear blade positioned downstream of the front blade in a transport direction of the substrate;
- a center blade positioned between the front blade and the rear blade; and
- an internal impurity removal space positioned between the center blade and the rear blade that removes impurities contained in a coating film of the slurry formed by passing by the center blade;
- the front blade and the center blade being configured to form a pool of the slurry, and
- a distance separating the rear blade and the substrate being set smaller than a distance separating the center blade and the substrate.

2. The die head apparatus according to claim **1**, wherein the center blade has a rotation application portion that applies a rotational force to the slurry in the pool.

3. The die head apparatus according to claim **2**, wherein the rotation application portion is configured from an irregularly shaped portion formed on a surface of the center blade facing the front blade, and
- the irregularly shaped portion has at least one of an inclined portion and a curved portion.

4. The die head apparatus according to claim **1**, wherein the center blade has a guide portion that guides the slurry constituting the coating film in a direction away from the substrate and toward the internal impurity removal space.

5. The die head apparatus according to claim **4**, wherein the guide portion is configured from an inclined portion formed on a surface of the center blade facing the rear blade.

6. The die head apparatus according to claim **1**, wherein the rear blade has a guide portion that guides impurities contained in the coating film to a surface of the coating film.

7. The die head apparatus according to claim **6**, wherein the guide portion of the rear blade is configured from an irregularly shaped portion formed on a surface of the rear blade facing the center blade,
- the irregularly shaped portion has at least one of an inclined portion and a curved portion, and
- a distance separating a start position of the irregularly shaped portion and the substrate is set to be larger than the distance separating the center blade and the substrate.

8. The die head apparatus according to claim **7**, wherein the curved portion of the irregularly shaped portion constituting the guide portion of the rear blade has a roller shape.

9. The die head apparatus according to claim **1**, wherein the internal impurity removal space is under negative pressure.

10. The die head apparatus according to claim **1**, wherein the impurities are bubbles or dust.

11. A laminated body forming apparatus comprising a plurality of the die head apparatuses according to claim **1** for forming a laminated body on the substrate that is transported, wherein
- the plurality of the die head apparatuses are arranged in series along the transport direction of the substrate, and the laminated body forming apparatus further comprises
- a plurality of external impurity removal spaces that remove impurities contained in a coating film of a slurry are respectively provided on downstream sides of the plurality of die head apparatuses in the transport direction.

12. The laminated body forming apparatus according to claim **11**, wherein
- the impurities are bubbles or dust.

13. The laminated body forming apparatus according to claim **1**, wherein
- the front blade has a triangular cross-sectional shape with a slanting edge that faces the center blade.

14. A coating method for forming a coating film by applying a slurry to a substrate that is transported by use of a die head apparatus, which has a front blade positioned to abut a flat surface of the substrate from a direction above the substrate, the substrate extending along a horizontal direction that is orthogonal to a vertical length of the front blade that extends in a direction of gravity, a rear blade positioned downstream of the front blade in a transport direction of the substrate, a center blade positioned between the front blade and the rear blade, and an internal impurity removal space positioned between the center blade and the rear blade, and in which a distance separating the rear blade and the substrate is set to be smaller than a distance separating the center blade and the substrate, the coating method comprising:

applying the slurry to the substrate to form the coating film with the center blade as the substrate passing through the slurry pool that is formed between the front blade and the center blade;

removing the impurities contained in the coating film of the slurry that is applied to the substrate as the substrate passes through the internal impurity removal space by floating the impurities to a surface of the coating film so that the impurities escape; and

forming the coating film with a uniform thickness by smoothing the surface of the coating film as the substrate passes the rear blade.

15. The coating method according to claim **14**, wherein the impurities are bubbles or dust.

16. A laminated body forming apparatus, comprising:

a plurality of die head apparatuses for forming a coating film by applying a slurry to a substrate that is transported, each of the die head apparatuses comprising,

a front blade,

a rear blade positioned downstream of the front blade in a transport direction of the substrate,

a center blade positioned between the front blade and the rear blade, and

an internal impurity removal space positioned between the center blade and the rear blade that removes impurities contained in a coating film of the slurry formed by passing by the center blade,

the front blade and the center blade being configured to form a pool of the slurry, and a distance separating the rear blade and the substrate being set smaller than a distance separating the center blade and the substrate,

the plurality of die head apparatuses being arranged in series along the transport direction of the substrate, and

the laminated body forming apparatus further comprises a plurality of external impurity removal spaces that remove impurities contained in a coating film of a slurry are respectively provided on downstream sides of the plurality of die head apparatuses in the transport direction,

the plurality of the die head apparatuses including

a first die head apparatus, and

a second die head apparatus that is adjacent to the first die head apparatus and that is positioned downstream of the first die head apparatus in the transport direction of the substrate,

a front blade of the second die head apparatus also serves as a rear blade of the first die head apparatus,

the external impurity removal space positioned between the first die head apparatus and the second die head apparatus also serves as an internal impurity removal space of the first die head apparatus, and

a distance separating the front blade of the second die head apparatus and the substrate is set to be smaller than a distance separating a center blade of the first die head apparatus and the substrate.

17. The laminated body forming apparatus according to claim **16**, wherein

the front blade of the second die head apparatus has a guide portion that guides impurities remaining in the coating film that has passed through the external impurity removal space to the surface of the coating film.

18. The laminated body forming apparatus according to claim **17**, wherein

the guide portion of the front blade of the second die head apparatus is configured from an irregularly shaped portion formed on a surface of the front blade that faces the center blade of the first die head apparatus,

the irregularly shaped portion of the front blade has at least one of an inclined portion and a curved portion, and

a distance separating the irregularly shaped portion of the front blade and the substrate is set to be greater than the distance separating the center blade of the first die head apparatus and the substrate.

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